(s, $OC(CH_3)_3$), 120.9, 121.7 (2d, C-4 and C-6), 124.2 (s, C-2), 125.3 (d, C-3′), 126.7, 127.1 (2d, C-2′ and C-5), 130.1 (d, C-3), 133.2 (s, C-1′), 136.8 (s, C-1), 150.2 (s, C-4′), 152.2 (s, NCOO), 170.1 (s, CON). Anal. Calcd for $C_{24}H_{32}N_2O_3$ (396.53): C, 72.70; H, 8.13; N, 7.06. Found: C, 72.73; H, 8.42; N, 6.96.

Lithiation of 1 with *n*-BuLi in Hexane Leading to Products 2a, 2b, and 2c. A solution of 1.00 g of 1 in 10 mL of hexane was cooled to 0 °C. After addition of 3.3 equiv of *n*-BuLi (2.5 M) at 0 °C the mixture was stirred at 2–5 °C for 45.5 h. Me_2S_2, 1.1 equiv, was added and the mixture allowed to warm to rt (1 h). After the mixture was quenched with brine the layers were separated, the organic layer was dried over Na_2SO_4 and filtered, and the solvent was evaporated. The crude mixture (0.96 g) was separated by column chromatography (petroleum ether (bp 40–60 °C)/ethyl acetate = 15/1). Besides recovered 1 (26%), products **2a**, **2b**, and **2c** were isolated.

***N*-Phenylpentanamide (2a).** Yield: 0.19 g (21%), colorless crystals. Mp: 60–61.5 °C (lit.[18] mp 60.5–61.5 °C). ^1H NMR: δ 0.95 (t, J = 7 Hz, 3 H, CH_3), 1.44 (sext, J = 7 Hz, 2 H, CH_2CH_3), 1.71 (sext, J = 7 Hz, 2 H, CH_2), 2.36 (t, J = 7 Hz, 2 H, $COCH_2$), 7.03–7.16 (m, 1 H, H-4), 7.18–7.42 (m, 3 H, H-3, H-5 and NH), 7.44–7.60 (m, 2 H, H-2 and H-6). ^{13}C NMR: δ 13.6 (q, CH_3), 22.2 (t, CH_2CH_3), 27.5 (t, CH_2), 37.4 (t, $COCH_2$), 119.7 (d, C-2), 124.0 (d, C-4), 128.8 (d, C-3), 137.8 (s, C-1), 171.4 (s, CO).

2-(Methylthio)-*N*-phenylpentanamide (2b). Yield 0.19 g (16%), colorless crystals. Mp: 80–82 °C. ^1H NMR: δ 0.95 (t, J = 7 Hz, 3 H, CH_3), 1.54 (sext, J = 7 Hz, 2 H, CH_2CH_3), 1.65–2.05 (m, 2 H, CH_2), 2.14 (s, 3 H, SCH_3), 3.35 (t, J = 7 Hz, 1 H, SCH), 7.03–7.19 (m, 1 H, H-4), 7.23–7.43 (m, 2 H, H-3 and H-5), 7.47–7.65 (m, 2 H, H-2 and H-6), 8.57 (br s, 1 H, NH). ^{13}C NMR: δ 13.7, 14.4 (2q, SCH_3 and CH_3), 20.7 (t, CH_2CH_3), 34.2 (t, CH_2), 52.4 (d, SCH), 119.7 (d, C-2), 124.4 (d, C-4), 129.0 (d, C-3), 137.7 (s, C-1), 170.1 (s, CO). Anal. Calcd for $C_{12}H_{17}NOS$ (223.34): C, 64.54; H, 7.67; N, 6.27. Found: C, 64.25; H, 7.45; N, 6.11.

***N*-(1,1-Dibutylpentyl)benzenamine (2c).** Yield: 0.27 g (19%), yellow oil. Bp: 78–84 °C (0.007–0.013 mmHg; Kugelrohr) (lit.[19] bp 186 °C (36 mmHg)). ^1H NMR: δ 0.89 (t, J = 7 Hz, 9 H, 3 × CH_3), 1.10–1.38 (m, 12 H, 3 × CH_2CH_2), 1.42–1.68 (m, 6 H, 3 × CCH_2), 3.30 (br s, 1 H, NH), 6.54–6.72 (m, 3 H, H-2, H-6, and H-4), 6.98–7.20 (m, 2 H, H-3 and H-5). ^{13}C NMR: δ 14.0 (q, CH_3), 23.0 (t, CH_2CH_3), 25.2 (t, CH_2), 36.2 (t, CCH_2), 66.5 (s, CCH_2), 115.6, 116.9 (2d, C-2 and C-4), 128.8 (d, C-3), 146.9 (s, C-1).

Registry No. 1, 3422-01-3; 2, 144303-96-8; **2a**, 10264-18-3; **2b**, 144304-01-8; **2c**, 35282-60-1; 3, 144303-97-9; 4, 144303-98-0; 5, 144303-99-1; Me_2S_2, 624-92-0; $ClCONEt_2$, 88-10-8; *t*-BuN=C=O, 1609-86-5; ClCON(Me)CH_2Ph(4-*t*-Bu), 144304-00-7; *n*-BuLi, 109-72-8; *t*-BuLi, 594-19-4.

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(19) Pornet, J.; Miginiac, L. *Bull. Soc. Chim. Fr.* **1974**, *5–6*, Pt. 2, 989.

Spontaneous Homopolymerization Competes with Diels–Alder Cycloaddition of 1-Aryl-1,3-butadienes to Dienophiles Containing a Leaving Group

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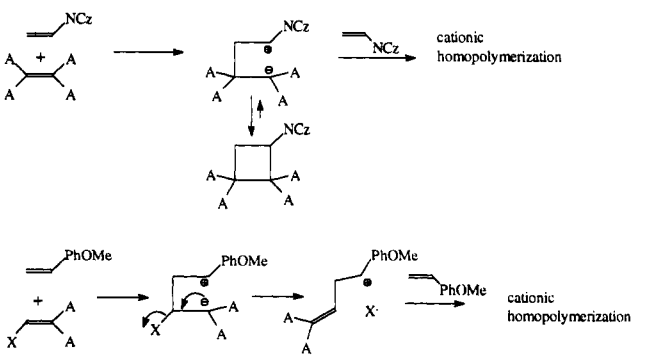
The competition between Diels–Alder cycloaddition and spontaneous concurrent polymerization was investigated in the reactions of 1-phenyl-1,3-butadiene (1) and 1-*p*-anisyl-1,3-butadiene (2) with electrophilic olefins. The reactions of 1 and 2 with electrophilic olefins trisubstituted with cyano and/or carbomethoxy groups gave only concerted [4 + 2] cycloaddition products. However, when olefins with a leaving group in the β-position were allowed to react with 1 and 2, cationic homopolymerization of the 1-arylbutadiene competed with the concerted cycloaddition. More polymer was formed with increased electrophilic character of the olefin and with better leaving groups. Formation of a 2-hexene-1,6-zwitterionic intermediate from the s-trans diene and the olefin, which can undergo elimination of the leaving group, is postulated. The resulting carbocation can then initiate cationic homopolymerization.

Introduction

The reactions of donor olefins with acceptor olefins are being extensively investigated in this laboratory.[1–4] Spontaneous chain polymerizations often compete with cycloadditions in these reactions. In the [2 + 2] cycloaddition of the very electron-rich *N*-vinylcarbazole with electrophilic olefins tetrasubstituted with cyano and/or carbomethoxy groups, the zwitterionic tetramethylene intermediate cyclizes or initiates the observed concurrent cationic homopolymerization of *N*-vinylcarbazole.[4] With less electron-rich donor olefins, such as *p*-methoxystyrene, cationic homopolymerization caused by electrophilic olefins only occurs if the latter has a leaving group in the β-position.[5–7] Again the proposed mechanism involves formation of a zwitterionic tetramethylene intermediate, here

Scheme I



NCz = N-carbazolyl, PhOMe = p-methoxyphenyl
A = CN or COOMe, X = leaving group

(1) Hall, H. K., Jr., *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.
(2) Hall, H. K., Jr.: Padias, A. B. *Acc. Chem. Res.* **1990**, *23*, 3.
(3) Hall, H. K., Jr.; Padias, A. B.; Pandya, A.; Tanaka, H. *Macromolecules* **1987**, *20*, 247.
(4) Gotoh, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4920.

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followed by expulsion of the leaving group leading to a carbocationic species. The latter initiates the cationic homopolymerization of the donor olefin, with the less nucleophilic leaving group acting as the counterion instead of the carbanion in the *N*-vinylcarbazole system (Scheme I).

To extend these studies to diene–olefin reactions, the reactions of 1-aryl-1,3-butadienes with trisubstituted electrophilic olefins with and without a β-leaving group are investigated in this paper. Again the focus will be on the competition between cycloaddition and spontaneous chain polymerization reactions. A new factor must be taken into account due to the nature of the reactants compared to the olefin–olefin reactions, namely that the diene–olefin cycloadditions can be concerted as they are orbital symmetry-allowed according to Woodward–Hoffmann rules. The dienes occur in an s-trans/s-cis equilibrium, and only the s-cis form can participate in the concerted [4 + 2] cycloadditions.

Results

The 1-aryl-1,3-butadienes used in this study were 1-phenylbutadiene (1) and 1-*p*-anisylbutadiene (2). The 1-arylbutadienes were checked for purity by GC and ^{1}H NMR and found to be both stereochemically pure (*E*)-1,3-dienes. The electrophilic olefins were methyl 3,3-dicyanoacrylate (3), dimethyl cyanofumarate (4), and trimethyl ethylenetricarboxylate (5), as well as the following olefins containing a potential β-leaving group: 2,2-dicyanovinyl chloride (6), 2,2-dicyanovinyl iodide (7), 2,2-dicyanovinyl tosylate (8), 2-carbomethoxy-2-cyanovinyl chloride (9), and 2-carbomethoxy-2-cyanovinyl iodide (10). From cyclic voltammetry measurements it is known that cyano substituents increase the electrophilicity of olefins compared to ester substituents.[8]

Control Experiments. The thermal stability of the reactants was checked under the reaction conditions used. In our earlier work it was established that the trisubstituted electrophilic olefins do not homopolymerize in the presence of free-radical initiators or spontaneously.[9]

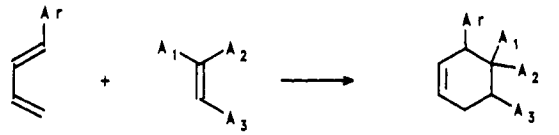
As far as the dienes are concerned, 1-phenyl-1,3-butadiene (1) does not spontaneously polymerize upon heating. This is in agreement with the data of Mulzer who reports quantitative dimerization at 130 °C after 48 h, but no polymer.[10] 1-*p*-Anisyl-1,3-butadiene (2) is stable at room temperature, but dimerizes after heating at 175 °C for 15 h with no oligomerization.

p-Toluenesulfonic acid or boron trifluoride etherate successfully initiated cationic homopolymerization of 1 to give high yields of poly(1-phenylbutadiene) in accordance with literature data.[11] 1-*p*-Anisylbutadiene also undergoes efficient homopolymerization with cationic initiators.

The arylbutadienes 1 and 2 were deliberately subjected to radical initiators but no polymer was obtained, in sharp contrast to a literature report.[12] Attempted free-radical-initiated copolymerizations of 1 and 2 with the trisubstituted electrophilic olefins 3 and 4 failed. Due to the high rate of cycloaddition at room temperature (see below), free-radical initiation at −50 °C using Et_3B and oxygen[13] was also used on these systems to allow copolymerization to compete, but again exclusively cycloadduct was obtained. Deliberately AIBN-initiated polymerization of acrylonitrile was inhibited by the presence of 1-*p*-anisyl-1,3-butadiene. The allylic radical formed may be excessively stabilized by the aryl group, prohibiting any radical-chain propagation reaction. Thus, the aromatic dienes act as a radical trap and inhibit free-radical (co)polymerizations.

Reactions of 1-Arylbutadienes with Trisubstituted Electrophilic Olefins without Leaving Groups. Reactions of electrophilic olefins trisubstituted with cyano and/or carbomethoxy groups with 1-phenyl-1,3-butadiene (1) and 1-*p*-anisyl-1,3-butadiene (2) in either dichloroethane or nitromethane solution gave exclusively [4 + 2] cycloadducts. Yields of the reactions are shown in Table I. Even though high concentrations or even bulk reaction conditions were used to allow polymerization to compete, no polymer was observed.

The reactions of either 1-arylbutadiene with these trisubstituted olefins always gave two isomers of the cycloadduct resulting from endo and exo addition with the same regiochemistry, as determined by ^{1}H and ^{13}C NMR analysis. The isomer ratios were determined by gas chromatography and are included in Table I.



1 Ar = Ph
2 Ar = *p*-MeOPh
E = COOMe

3 $A_1 = A_2 = CN$, $A_3 = E$
4 $A_1 = A_3 = E$, $A_2 = CN$
5 $A_1 = A_2 = A_3 = E$

11 Ar = Ph, $A_1 = A_2 = CN$, $A_3 = E$
12 Ar = Ph, $A_1 = A_3 = E$, $A_2 = CN$
13 Ar = Ph, $A_1 = A_2 = A_3 = E$
14 Ar = *p*-MeOPh, $A_1 = A_2 = CN$, $A_3 = E$
15 Ar = *p*-MeOPh, $A_1 = A_3 = E$, $A_2 = CN$
16 Ar = *p*-MeOPh, $A_1 = A_2 = A_3 = E$

The predominant isomer of 4,4,5-tricarbomethoxy-3-phenylcyclohex-1-ene (13), obtained from cycloaddition of 1 with the triester olefin 5, was thoroughly investigated by ^{1}H NMR by proton homodecoupling experiments. Irradiation of H_{6a} and H_{6e} in the major isomer of adduct 13 shows that H_5 is coupled only to these two hydrogens. The doublet from H_3 is simplified to a singlet on irradiation of H_2, indicating that the methine C_3 is adjacent to the quaternary carbon C_4 (with two ester substituents) and to C_2 carrying the vinyl proton H_2. The stereochemistry at C_3 and C_5 was determined by the coupling constants: $J_{5,6a}$ is approximately 11 Hz and $J_{5,6e}$ is approximately 7.5 Hz, which is indicative of axial–axial and equatorial–axial coupling, respectively. Thus, H_5 is in the axial position. Homoallylic coupling constants $J_{3,6a}$ and $J_{3,6e}$ were found to be 3.5 and 1.5 Hz, respectively. Comparison with Barfield's calculated coupling constants indicates that H_3 is axial.[14] Therefore, the major isomer of 13 has the donor

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(9) Hall, H. K., Jr.; Daly, R. C. *Macromolecules* **1975**, *8*, 22.
(10) Mulzer, J.; Kuehl, U.; Huttner, G.; Evertz, K. *Chem. Ber.*, **1988**, *121*, 2231. In the dimerization of 1-arylbutadiene derivatives, the nonconcerted nature of the [4 + 2] cycloaddition was proven based on stereochemical and kinetic data.
(11) Masuda, T.; Otsuki, M.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1385.
(12) Lewis, D. H.; Kneisel, R. C.; Ponder, B. W. *Macromolecules* **1973**, *6*, 660.
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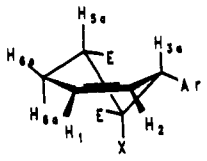
Table I. Reactions of 1-Aryl-1,3-butadiene with Trisubstituted Olefins Lacking β-Leaving Groups

olefins[a]	solvent[b]	concn (M)	time (h)	temp (°C)	[4+2] adduct[d] isomer ratio	[4+2] adduct[d] % yield
Reactions of 1-Phenyl-1,3-butadiene (1)						
 3		bulk	2	60	11	62
	DCE	1.9	3.5	0	11 4:1	71
	DCE	0.8	3.5	0	11	73
 4		bulk	7	27	12	85
	DCE	1.9	5	0	12 5:1	57
	DCE	0.8	16	0	12	61
 5		bulk	44	70	13	62
	DCE	1.9	144	70	13 1:1	86
	c	bulk	44	70	13	60
	DCE[c]	1.9	144	70	13	81
Reactions of 1-*p*-Anisyl-1,3-butadiene (2)						
 3		bulk	20	27	14	85
	DCE	1.9	1.5	0	14 2:1	76
	DCE	0.8	20	27	14	88
	CH_3NO_2	1.9	16	27	14	91
 4		bulk	20	27	15	67
	DCE	1.9	1.5	0	15 1:1	68
	DCE	0.8	20	27	15	77
	CH_3NO_2	1.9	16	27	15	76
 5	DCE	1.9	48	150	16	21
	c	bulk	20	80	16 1:1	18
	DCE[c]	1.9	20	80	16	33
	CH_3NO_2	1.9	16	80	16	83

[a] E = COOMe. [b] DCE = 1,2-dichloroethane. [c] AIBN added. [d] No polymer was formed in any of these reactions; reported yields are isolated yields.

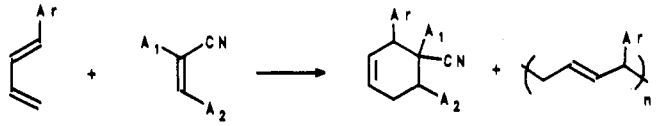
substituent on C_3 and the ester group on C_5 cis to each other in equatorial positions, which results from exo addition. The coupling constants of the other cycloadducts were also determined but not in as great detail. The adduct **12** of **1** with dimethyl cyanofumarate **4** consists of two isomers, both with the ester groups trans to each other as in the olefin, indicating that the reaction proceeds without loss of stereochemistry.



major isomer **12** X = CN
major isomer **13** X = E
E = COOMe

Reactions of 1-Arylbutadienes with Trisubstituted Olefins Containing a β-Leaving Group. The reactions of olefins **6–10** with the 1-arylbutadienes **1** and **2** were done at high concentration or in bulk to favor possible polymerization. As shown in Table II, homopolymer of the 1-arylbutadiene as well as cycloadduct is obtained. In the extreme case of 2,2-dicyanovinyl tosylate only homopolymer is obtained and no cycloadduct. Two isomers (exo and endo) of the cycloadducts with the same regiospecificity are always observed. For the cycloadducts of 2-carbomethoxy-2-cyanovinyl chloride (**9**) and iodide (**10**), the trans configuration between the ester and halogen substituent is retained. The yield of homopolymer and its molecular weight increase with leaving group ability: chloride < iodide < tosylate.

The homopolymerization of the arylbutadienes is cationic in nature, because the control experiments showed that cationic, but not free-radical, homopolymerization can occur. To ensure that these polymerizations are not initiated by adventitious acidic impurities, these experiments were repeated in the presence of a hindered base. 2,6-Di-*tert*-butyl-4-methylpyridine (DBMP) will react with a proton, but is too sterically hindered to react with a carbocation, and thus does not interfere with the growing carbocationic center.[15,16] As shown in Table II, the po-



1 Ar = Ph
2 Ar = *p*-MeOPh

6 A_1 = CN, A_2 = Cl
7 A_1 = CN, A_2 = I
8 A_1 = CN, A_2 = OTos
9 A_1 = E, A_2 = Cl
10 A_1 = E, A_2 = I

E = COOMe

17 Ar = Ph, A_1 = CN, A_2 = Cl
18 Ar = Ph, A_1 = CN, A_2 = I
19 Ar = Ph, A_1 = E, A_2 = Cl
20 Ar = Ph, A_1 = E, A_2 = I
21 Ar = *p*-MeOPh, A_1 = CN, A_2 = Cl
22 Ar = *p*-MeOPh, A_1 = E, A_2 = Cl
23 Ar = *p*-MeOPh, A_1 = E, A_2 = I

lymerizations did proceed in the presence of the hindered base. A control experiment was carried out in a NMR tube containing 1-phenyl-1,3-butadiene (**1**), DBMP, and 2,2-dicyanovinyl chloride (**6**) in a 20:1:1 mole ratio. A slight shift can be observed for the vinyl proton on **6** indicating some complexation between DBMP and **6**. After 24 h

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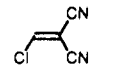
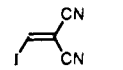
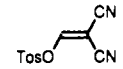
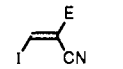
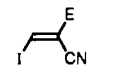
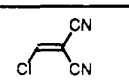
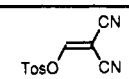
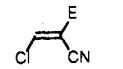
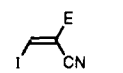
Table II. Reactions of 1-Aryl-1,3-butadiene with Olefins Having β-Leaving Groups

olefins[a]	solvent[b]	concn (M)	[4+2] adduct			homopolymer		
				isomer ratio	% yield	% yield	M_n	M_w
Reaction of 1-Phenyl-1,3-butadiene (1)								
 6	DCE	0.9	17		47	0		
	DCE	1.6	17	9:1	43	2		
	CH_3NO_2	1.6	17		39	4		
		bulk	17		54	6	800	900
	CH_2Cl_2/base	1.6			c	5		
 7	DCE	1.6	18	2:1	46	16	1800	2100
	CH_3NO_2	1.6	18		34	25		
 8	DCE	0.2			0	37	1800	2000
	CH_3NO_2	0.9			0	54		
	CH_2Cl_2/base	1.6			0	40		
 9	DCE	1.6	19	2:1	77	trace		
	CH_3NO_2	1.6	19		80	trace		
 10	DCE	2	20	1:25	79	trace		
	CH_3NO_2	2	20		87	2		
Reactions of 1-*p*-Anisyl-1,3-butadiene (2)								
 6	DCE	2	21	3:1	80	5	1900	2000
	CH_2Cl_2/base	2			c	4		
 8	DCE	2			0	95		
	DCE	d			0	100	2010	3300
	CH_2Cl_2/base	1.8			0	72		
 9	DCE	2	22	1:1	88	3	655	860
 10	DCE	2	23	3:1	74	13	655	865

[a] Reaction conditions: 27 °C, 16 h. E = COOMe, Tos = $CH_3C_6H_4SO_2$. [b] DCE = 1,2-dichloroethane. Base = 2,6-di-*tert*-butyl-4-methylpyridine (5 mol % vs diene). [c] Cycloadduct yield not determined. [d] Concentration of 2 is 2 M, 8 at 0.2 M: molar ratio 2:8 = 10:1.

there was no evidence of DBMP hydrochloride salt in the NMR spectrum, but homopolymerization of 1 did proceed.

Discussion

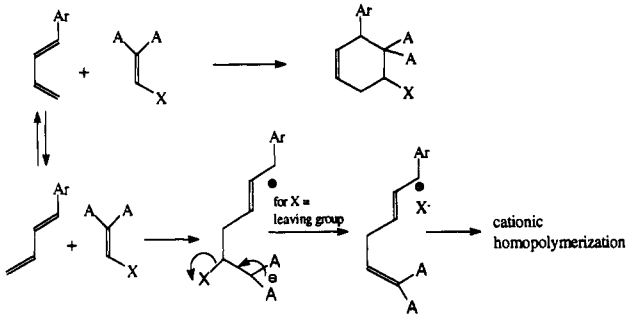
In the reactions of 1-arylbutadienes with cyano- and carbomethoxy-substituted olefins, only cycloadducts are obtained. Homopolymers do not form, while copolymers (putative radical mechanism) are not possible as established by the control experiments. The cycloadducts comprise only the expected pairs of isomers without any loss of stereochemistry in the case of dimethyl cyanofumarate. These reactions are typical Diels–Alder reactions in every respect with no side products.

More interesting results are observed in the reactions of 1-arylbutadienes 1 and 2 with the trisubstituted olefins containing a β-leaving group. Both [4 + 2] cycloadducts and homopolymer of the electron-rich diene are obtained. The cycloadducts are again obtained as the expected two isomers. No loss of stereochemistry is observed in the cycloadditions involving asymmetric dienophiles, implying a concerted cycloaddition. The polymerization is cationic in nature. Better leaving group ability as well as greater acceptor power of the electrophilic olefins results in more homopolymer. The 2,2-dicyano-substituted olefins are much more reactive than the 2-carbomethoxy-2-cyano-substituted ones.

To verify that the cationic polymerization of the diene is not initiated by acidic impurities, the experiments were repeated in the presence of DBMP. Hydrolysis of the electrophilic olefin or the cycloadduct can be a source of acid. However the cationic polymerization proceeds in the presence of DBMP, and no DBMP hydrochloride can be detected. The somewhat lower yields and slower reaction in the presence of DBMP are ascribed to complexation of the olefin by DBMP, reducing its electrophilic character.

The cycloadducts form from concerted reaction of the s-cis form of the diene with the electrophilic olefin, in accordance with orbital symmetry rules. However, the homopolymer is evidence for the existence of an initiating carbocationic species. The proposed mechanism is based on the postulated mechanism in the [2 + 2] case (Scheme I),[5-7] namely reaction of the s-trans form of the diene with the olefin resulting in a 2-hexene-1,6-zwitterion as shown in Scheme II. As the leaving group departs, a cationic

Scheme II



Ar = phenyl or p-methoxyphenyl
A = CN or COOMe, X = CN, COOMe or leaving group

intermediate is formed which initiates homopolymerization of the electron-rich 1-arylbutadiene. This interpretation explains the correlation of homopolymer yield with the leaving group ability. In addition to being the best leaving group, the tosylate ion is the least nucleophilic and is most suitable as counterion in the cationic propagation reaction, so it favors both higher yield and increased molecular weight.

Stepwise [4 + 2] cycloadditions via zwitterionic intermediates have been described in the literature for diene/dienophile pairs with large $HOMO_{diene} - LUMO_{dienophile}$ separations as well as unfavorable steric factors.[17] An example is the stepwise reaction of 1,1-diaryl-1,3-butadienes with tetracyanoethylene TCNE,[18] while the cycloadditions of the less sterically hindered 1-aryl-1,3-butadienes with TCNE are all presumed to be concerted independent of the para substituent of the aryl group.[19] The latter is in agreement with our work in which no stereochemical evidence is found for a stepwise cycloaddition. Moreover, the electrophilic olefins used in this study are less powerful electrophiles than TCNE.

In conclusion, we have shown that cationic homopolymerization, initiated by a postulated cationic intermediate, can compete with [4 + 2] cycloaddition in reactions of 1-arylbutadienes with dienophiles containing a leaving group. This is one study in an ongoing investigation of the competition between cycloaddition and polymerization in diene/olefin reactions.[20]

Experimental Section

Instrumentation. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-250 nuclear magnetic resonance spectrometer at 250 MHz. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus and are corrected. Gas chromatograms were obtained using a Varian 3300 GC with an OV-101 column. SEC data were obtained using a Shodex 804 and 805 column in chloroform as eluent versus polystyrene standards. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Solvents. 1,2-Dichloroethane and nitromethane were dried over CaH_2 and distilled before use.

Reactants. 1-Phenyl-1,3-butadiene was prepared by the Wittig reaction on cinnamaldehyde according to the procedure of Mulzer.[21] 1-*p*-Anisyl-1,3-butadiene was prepared according to the procedure of Low.[22] Electrophilic olefins were synthesized according to literature procedures: methyl 3,3-dicyanoacrylate (**3**),[23] dimethyl cyanofumarate (**4**),[3] trimethyl ethylenetricarboxylate (**5**),[24] 2,2-dicyanovinyl chloride (**6**),[25] 2,2-dicyanovinyl iodide (**7**),[6] 2,2-dicyanovinyl tosylate (**8**),[7] 2-cyano-2-(methoxycarbonyl)vinyl chloride (**9**),[26] and 2-cyano-2-(methoxycarbonyl)vinyl iodide (**10**).[6] 2,6-Di-*tert*-butyl-4-methylpyridine was purchased from Aldrich and purified by distillation over potassium hydroxide.

Typical Reaction Procedure. 1-*p*-Anisyl-1,3-butadiene (0.5 g, 3.13 mmol) was dissolved in 0.31 mL of dichloroethane and put in one arm of a Y-shaped tube equipped with a vacuum Teflon valve. Methyl 3,3-dicyanoacrylate (0.43 g, 3.13 mmol) was dissolved in 0.3 mL of dichloroethane and put in the other arm of the Y-tube. The solutions were degassed using the freeze–thaw method and placed under Ar. Both reactants were allowed to warm at 0 °C and mixed. The reaction mixture was stirred for 1.5 h. Methanol was added and the resulting precipitate filtered. This precipitate is the polymer which was analyzed by SEC. The filtrate was concentrated, and the cycloadduct was isolated. The cycloadducts (except **21**) were purified by silica gel column chromatography using hexane/ethyl acetate mixtures as eluent before analysis. The isolated yields are summarized in Table I and II.

Control Polymerizations. 1-Phenylbutadiene (**1**) is stable under the reaction conditions used: 70 °C for several days. 1-*p*-Anisylbutadiene (**2**) dimerized when heated at 175 °C for 15 h. Blank experiments using AIBN as initiator at 70 °C did not yield any polymer of **1** or **2** after 24 h. Both **1** and **2** undergo efficient cationic homopolymerization (see above), and the polymer structure is the same as for the polymers obtained in this study.

Attempted free-radical-initiated copolymerizations of the arylbutadienes with the olefins **3**–**5** using AIBN at 80 °C were also unsuccessful. An AIBN-initiated polymerization of 1-*p*-anisyl-1,3-butadiene and trimethyl ethylenetricarboxylate (**5**) (much slower cycloaddition) gave no copolymer, only cycloadduct. In an attempt to slow down the cycloaddition reaction, a low-temperature free-radical initiating system was used. 1-*p*-Anisyl-1,3-butadiene was mixed in toluene at −50 °C with triethylborane, oxygen,[11] and methyl dicyanoacrylate, but the formed precipitate proved to be exclusively the [4 + 2] cycloadduct and no polymer was obtained. The same results were obtained using dimethyl cyanofumarate as the electrophilic olefin.

Physical Data for the Cycloadducts. 4,4-Dicyano-5-(methoxycarbonyl)-3-phenylcyclohex-1-ene (11): mp 108–109 °C; IR (KBr, cm^{-1}) 2249 (C≡N), 1740 (C=O), 1601 (Ph); ^1H NMR ($CDCl_3$) mixture of two isomers δ 2.5–2.9 (2 H, H_{6a}, H_{6e}, m), 3.2, (H_{5e} minor isomer, dd, $J_{5e,6a}$ = 8.9 Hz, $J_{5e,6e}$ = 6.1 Hz) 3.35 (1 H, H_{5a} major isomer, dd, $J_{5a,6a}$ = 11.5 Hz, $J_{5a,6e}$ = 5.9 Hz), 3.8, 3.85 (3 H, s), 4.0, 4.3 (1 H, H_3, m), 5.8 (1 H, H_1, m), 6.1 (1 H, H_2, m), 7.4 (5 H, m); ^{13}C NMR ($CDCl_3$, two isomers) δ 26.3, 26.4 (C_6), 41.1, 47.3 (C_4), 42.1, 47.3 (C_5), 47.9, 50.2 (C_3), 53.6 (OCH_3), 112.4, 115.3 (CN), 125.0, 126.5, 126.8, 127.7, 129.3, 129.9, 130.0, 130.8 (C_1, C_2, C_2', C_3', C_4'), 135.3, 136.0 (C_1'), 170.4 (C=O). Comment: C′ = aromatic carbon. Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.97; H, 5.19; N, 10.39.

4-Cyano-4,5-bis(methoxycarbonyl)-3-phenylcyclohex-1-ene (12): mp 133.5–134.5 °C; IR (KBr, cm^{-1}) 2243 (C≡N) 1745, 1725 (C=O); ^1H NMR (major isomer) ($CDCl_3$) δ 2.5 (1 H, H_{6a}, m, $J_{6a,6e}$ = 18.4 Hz, $J_{6a,5a}$ = 12.2 Hz), 2.8 (1 H, H_{6e}, m, $J_{6e,5a}$ = 5.8 Hz), 3.2 (1 H, H_{5a}, dd), 3.55 (3 H, s), 3.69 (3 H, s), 4.1 (1 H, H_{3a}, broad s), 5.8 (1 H, H_1, m), 6.1 (1 H, H_2, m), 7.1–7.3 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 26.3 (C_6), 38.5 (C_5), 49.2 (C_3), 49.4 (C_4), 52.2, 52.9 (OCH_3), 117.9 (CN), 124.9, 126.3, 128.5, 129.2, (C_1, C_2, C_2', C_3', C_4'), 166.8,

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172.2 (C=O). Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.72; N, 4.68. Found: C, 68.14, H, 5.72, N, 4.70.

4,4,5-Tris(methoxycarbonyl)-3-phenylcyclohex-1-ene (13): mp 103–104 °C; IR (KBr, cm^{-1}) 1751, 1735, 1724 (C=O); ^1H NMR (major isomer) ($CDCl_3$) δ 2.5 (1 H, H_{6a}, m, $J_{6a,6e}$ = 18 Hz, $J_{6a,5a}$ = 10.5 Hz, $J_{6a,3a}$ = 3.5 Hz, $J_{6a,2}$ = 2.3 Hz), 2.78 (1 H, H_{6e}, m, $J_{6e,5a}$ = 7.5 Hz, $J_{6e,3a}$ = 1.5 Hz) 3.3 (3 H, OCH_3, s), 3.35 (1 H, H_{5a}, dd), 3.7 (3 H, OCH_3, s), 3.8 (3 H, OCH_3, s), 4.4 (1 H, H_{3a}, m), 5.7 (1 H, H_1, m, $J_{1,2}$ = 10.5 Hz), 5.9 (1 H, H_2, m), 7.1–7.3 (5 H, arom, m); ^{13}C NMR ($CDCl_3$) δ 25.9 (C_6), 39.0 (C_5), 46.9 (C_3), 51.7, 52.0, 52.8 (OCH_3), 60.0 (C_4), 125.9, 126.7, 127.4 (C_2', C_3', C_4'), 128.1, 129.6 (C_1, C_2), 139.2 (C_1'), 169.7, 169.8, 173.2 (C=O). Anal. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 64.89; H, 5.90.

4,4-Dicyano-5-(methoxycarbonyl)-3-(*p*-methoxyphenyl)-cyclohex-1-ene (14): mp 162–4 °C. IR (KBr, cm^{-1}) 2965 (CH), 2240 (C≡N), 1750 (C=O), 1600 (Ph), 1525 (OCH_3); ^1H NMR major isomer ($CDCl_3$) δ 2.6–2.8 (2 H, H_{6a} and H_{6e}, m), 3.3 (1 H, H_{5a}, $J_{5a,6a}$ = 11.4 Hz, $J_{5a,6e}$ = 6.0 Hz, dd), 3.8 (3 H, s), 3.85 (3 H, s), 4.0 (1 H, H_{3a}, broad s) 5.75 (1 H, H_1, m), 6.05 (1 H, H_2, m), 6.9 (2 H, d), 7.35 (2 H, d); ^{13}C NMR ($CDCl_3$) δ 25.8 (C_6), 40.8 (C_4), 46.6 (C_5), 49.0 (C_3), 53.0 (OCH_3(ester)), 55.2 (OCH_3(Ar)), 111.9, 114.8 (CN), 114.1 (C_2'), 126.3, 126.9 (C_1, C_2), 127.3 (C_1'), 130.5 (C_3'), 160.2 (C_4'), 169.6 (C=O). Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.97; H, 5.45; N, 9.46. Found: C, 68.45; H, 5.33; N, 9.38.

4-Cyano-4,5-bis(methoxycarbonyl)-3-(*p*-methoxyphenyl)cyclohex-1-ene (15): IR (KBr, cm^{-1}) 3000 (=CH) 2950 (CH), 1720 (C=O), 1595 (Ph), 1530 (OCH_3); ^1H NMR (mixture of two isomers) ($CDCl_3$) δ 6.8–7.2 (4 H, m), 6.02 (1 H, H_2, m), 5.74 (1 H, H_1, m), 4.13, 3.94 (1 H, 2 isomers broad m), 3.79, 3.77, 3.73, 3.72, 3.71, 3.69 (9 H, 6s), 3.5, 3.2 (1 H, H_5 in 2 isomers, m), 2.8 (1 H, H_{6e}, m), 2.55 (1 H, H_{6a}, m); ^{13}C NMR ($CDCl_3$) δ 172.2, 171.0, 159.3, 159.2 (C=O), 169.0, 166.0 (C'_4), 130.1, 129.8, 129.3, 127.2, 126.7, 125.0, 113.5, 113.2 (C_1, C_2, C'_2, C'_3), 128.9, 127.4 (C'_1), 117.8, 115.3 (CN), 54.8, 53.8, 52.8, 52.7, 52.2 (OCH_3), 52.2, 49.2 (C_4), 48.3, 45.3 (C_3), 45.3, 38.2 (C_5), 26.1, 25.6 (C_6). Anal. Calcd for $C_{18}H_{19}NO_5$: C, 65.65; H, 5.77, N, 4.26. Found: C, 65.72; H, 5.63; N, 4.07.

4,4,5-Tris(methoxycarbonyl)-3-(*p*-methoxyphenyl)cyclohex-1-ene (16): mp 117–118 °C; IR (KBr, cm^{-1}) 3075 (=CH), 2950 (CH), 1750 (C=O), 1700 (C=O), 1615 (Ph), 1525 (OCH_3); ^1H NMR ($CDCl_3$) δ 2.4–2.6 (1 H, H_{6a}, m), 2.7–2.85 (1 H, H_{6e}, m), 3.3 (3 H, s), 3.65 (3 H, s), 3.7 (1 H, H_5, m), 3.77 (3 H, s), 4.35 (1 H, H_{3a}, broad d), 5.7 (1 H, H_1, m), 5.9 (1 H, H_2, m), 6.8 (2 H, d), 7.1 (2 H, d); ^{13}C NMR ($CDCl_3$) δ 25.9 (C_6), 39.2 (C_5), 46.2 (C_3), 51.8, 51.9, 52.7 (OCH_3), 55.1 (OCH_3, (Ar)), 59.9 (C_4), 113.4 (C_3'), 125.5, 127.0, 130.6 (C_2, C_1, C_2'), 130.9 (C_1'), 169.7, 173.2 (C=O). Anal. Calcd for $C_{19}H_{22}O_7$: C, 62.98; H, 6.12. Found: C, 63.23; H, 6.15.

5-Chloro-4,4-dicyano-3-phenylcyclohex-1-ene (17): mp 110–1 °C; IR (KBr, cm^{-1}) 3029 (=CH), 2261 (C≡N), 1601 (Ph); ^1H NMR (major isomer) ($CDCl_3$) δ 2.75–3.01 (2 H, H_{6a} and H_{6e}, m), 4.1 (1 H, H_{3a}, m), 4.5 (1 H, H_{5a}, $J_{5a,6a}$ = 10.3 Hz, $J_{5a,6e}$ = 6.2 Hz, dd), 5.7–6.0 (2 H, H_1 and H_2, m), 7.44 (5 H, s); ^{13}C NMR ($CDCl_3$) δ 32.7 (C_6), 48.9 (C_4), 50.6 (C_3), 56.4 (C_5), 110.9, 113.7 (C_1, C_2), 125.7, 126.9, 129.0 (C'_2, C'_3, C'_4), 135.1 (C'_1). Anal. Calcd for $C_{14}H_{11}ClN_2$: C, 69.28; H, 4.57; N, 11.54. Found: C, 69.42; H, 4.45; N, 11.37.

4,4-Dicyano-5-iodo-3-phenylcyclohex-1-ene (18): mp 122–123 °C; IR (KBr, cm^{-1}) 3039 (=CH), 2247 (C≡N), 1599 (Ph); ^1H NMR (two isomers) $CDCl_3$ δ 3.0–3.4 (2 H, H_6, m), 4.1, 4.3 (1 H, H_3, 2s), 4.6 (1 H, H_5, m), 5.9–6.0 (2 H, H_1 and H_2, m), 7.4 (5 H, m). Anal. Calcd for $C_{14}H_{11}IN_2$: C, 50.32; H, 3.32, N, 8.38. Found: C, 50.60, H, 3.33, N, 8.32.

5-Chloro-4-cyano-4-(methoxycarbonyl)-3-phenylcyclohex-1-ene (19): mp 123–5 °C; IR (KBr, cm^{-1}) 3032 (=CH), 2240 (C≡N), 1757 (C=O), 1598 (Ph); ^1H NMR (two isomers) ($CDCl_3$) δ 2.7–3.1 (2 H, H_6, m), 3.51, 3.72 (3 H, 2s), 4.2–4.3 (1 H, H_3, m), 4.5–4.6 (1 H, H_5, m) 5.7–6.1 (2 H, H_1, H_2, m), 7.1–7.4 (5 H, m). Anal. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 65.27; N, 5.08. Found: C, 65.27; H, 4.97; N, 5.09.

4-Cyano-5-iodo-4-(methoxycarbonyl)-3-phenylcyclohex-1-ene (20): mp 140–1 °C; IR (KBr, cm^{-1}) 3027 (=CH), 2242 (C≡N), 1756 (C=O); ^1H NMR (two isomers) ($CDCl_3$) δ 2.9–3.3 (2 H, H_6, m), 3.50, 3.71 (3 H, 2 s, 4.21 (1 H, H_3, m), 4.56 (dd, H_5 major isomer, J = 7.2, 10.3 Hz), 4.70 (dd, H_5 minor isomer, J = 7.0, 12.2 Hz), 5.8–6.0 (2 H, H_1 and H_2, m), 7.1–7.5 (5 H, m). Anal. Calcd for $C_{15}H_{14}INO_2$: C, 49.06; H, 3.84; N, 3.81. Found: C, 48.93; H, 3.90; N, 3.80.

5-Chloro-4,4-dicyano-3-(*p*-methoxyphenyl)cyclohex-1-ene (21). This cycloadduct could not be obtained pure. It was always contaminated by oligomers. It could not be recrystallized (mixture of isomers) and decomposed on silica gel: ^1H NMR (two isomers) ($CDCl_3$) δ 2.7–3.1 (2 H, H_6, m), 3.83, 3.82 (3 H, 2s), 4.07, 4.17 (1 H, H_3, broad s), 4.5 (1 H, H_5, m), 5.75 (1 H, H_1, m), 5.97 (1 H, H_2, m), 7.2–7.3 (4 H, m).

5-Chloro-4-cyano-4-(methoxycarbonyl)-3-(*p*-methoxyphenyl)cyclohex-1-ene (22): ^1H NMR (two isomers) ($CDCl_3$) 2.8–3.1 (2 H, H_6, m), 3.57, 3.74, 3.79, 3.80 (6 H, 4s), 4.13, 4.19 (1 H, H_3, 2m), 4.49 (dd, H_5 isomer 1, J = 10.6, 6.0 Hz), 4.59 (dd, H_5 isomer 2, J = 9.0, 8.0 Hz), 5.80 (1 H, H_1, m), 5.95 (1 H, H_2, m), 6.8–7.3 (4 H, 2AB systems).

4-Cyano-5-iodo-4-(methoxycarbonyl)-3-(*p*-methoxyphenyl)cyclohex-1-ene (23): ^1H NMR (two isomers) ($CDCl_3$) δ 3.0–3.15 (1 H, H_6, m), 3.55, 3.73, 3.79, 3.81, 3.83 (6 H, s), 4.17 (1 H, H_3, m), 4.54 (dd, H_5 major isomer, J = 10.1, 7.1 Hz), 4.68 (dd, H_5 minor isomer, J = 6.1, 11.0 Hz), 5.8 (2 H, H_1 and H_2, m), 6.8–7.2 (4 H, 2AB systems).

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Supplementary Material Available: ^1H NMR spectra for cycloadducts 21–23 (3 pages). This material is contained in many 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.