yields of 23%, 27%, and 31%.

Isomer A: mp 90–91 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 7.92–7.88 (m, 2 H), 7.62–7.50 (m, 3 H), 5.49 (d, J = 3 Hz, 1 H), 3.23–3.13 (m, 1 H), 3.09 (br s, 1 H), 2.88 (br s, 1 H), 2.78 (br s, 1 H), 2.15–1.20 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 163.56, 141.03, 133.12, 129.09, 128.16, 120.64, 65.88, 62.38, 45.92, 44.61, 42.14, 38.74, 38.20, 32.13, 31.94, 24.71 ppm; mass spectrum, calcd (M^+) *m/e* 300.1184, obsd 300.1193.

Isomer B: ^{1}H NMR ($CDCl_3$) δ 8.03–7.80 (m, 2 H), 7.73–7.41 (m, 3 H), 5.45 (d, J = 4 Hz, 1 H), 3.40–3.00 (m, 2 H), 2.80 (br s, 1 H), 2.40 (br s, 1 H), 2.20–1.10 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 166.91, 140.06, 133.26, 129.18, 128.21, 116.95, 65.73, 62.04, 48.01, 46.02, 42.38, 39.08, 38.88, 31.60, 29.42, 24.90 ppm.

Isomer C: mp 119–120 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 7.90–7.84 (m, 2 H), 7.63–7.50 (m, 3 H), 5.38 (d, J = 2.6 Hz, 1 H), 3.75–3.62 (m, 1 H), 3.07 (br s, 1 H), 2.89 (d, J = 2.5 Hz, 1 H), 2.28 (d, J = 3 Hz, 1 H), 2.00–1.18 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 163.90, 140.64, 133.16, 129.04, 128.16, 111.85, 65.44, 62.43, 49.90, 49.03, 42.33, 39.42, 38.83, 31.45, 29.80, 24.66 ppm; mass spectrum, calcd (M^+) *m/e* 300.1184, obsd 300.1193.

Desulfonylation of the Phenyl Vinyl Sulfone Adducts 24. The general 6% sodium amalgam reduction procedure described above was applied independently to isomers A–C. Each of these reactions delivered only olefinic hydrocarbon **9** in isolated yields of 25%, 20%, and 87%, respectively.

Phenyl Vinyl Sulfone Addition to 25 $\rightleftarrows$ 26. A mixture of **25** (0.50 g, 3.42 mmol), phenyl vinyl sulfone (0.58 g, 3.45 mmol), and toluene (3 mL) was placed in a sealed heavy-walled Pyrex tube and heated at 107 °C for 2 days. The solvent was evaporated, and the residue was subjected to MPLC purification (elution with 10% ethyl acetate in petroleum ether). There was isolated 0.35 g (33%) of linear adduct **27** and 0.54 g (50%) of angular adduct **28**.

For **27**: mp 128–129.5 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 8.00–7.80 (m, 2 H), 7.67–7.40 (m, 3 H), 3.10–2.63 (m, 6 H), 2.40–2.10 (m, 1 H), 1.90–1.03 (series of m, 7 H), 0.63 (d, J = 6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 155.65, 150.36, 140.45, 133.32, 129.24, 128.22, 66.85, 56.46, 55.35, 49.33, 46.75, 41.27, 40.93, 31.61, 25.49, 25.25, 11.75 ppm; mass spectrum, calcd (M^+) *m/e* 314.1340 obsd 314.1349.

Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.46; H, 7.08.

For **28**: mp 107–108 °C (from hexanes); ^{1}H NMR ($CDCl_3$) δ 7.87–7.83 (m, 2 H), 7.63–7.50 (m, 3 H), 5.19 (s, 1 H), 3.50 (dd, J = 9.6, 5.1 Hz, 1 H), 2.79 (d, J = 3.6 Hz, 1 H), 2.19 (d, J = 3.6 Hz, 1 H), 1.87–1.90 (m, 2 H), 1.80–1.64 (m, 2 H), 1.62–1.54 (m, 1 H), 1.39 (s, 3 H), 1.47–1.21 (m, 5 H); ^{13}C NMR ($CDCl_3$) 163.12, 141.37, 133.12, 128.99, 128.41, 116.95, 70.10, 60.93, 57.79, 57.63, 41.95, 39.47, 38.74, 34.13, 31.51, 24.61, 19.32 ppm; mass spectrum, calcd (M^+) *m/e* 314.1340, obsd 314.1346.

4-Methyl-*anti*-tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene (29). By use of the general procedure described above, reduction of **28** (300 mg, 0.95 mmol) gave 40 mg (24%) of **29** after preparative VPC purification (12 ft × 0.25 in. column, 15% SE-30, 170 °C) together with 200 mg (67%) of recovered starting material.

For **29**: ^{1}H NMR ($CDCl_3$) δ 5.12 (s, 1 H), 2.73 (br s, 1 H), 2.24 (br s, 1 H), 1.98 (td, J = 10, 2 Hz, 1 H), 1.25 (s, 3 H), 1.74–1.02 (series of m, 11 H); ^{13}C NMR ($CDCl_3$) 162.40, 120.55, 62.29, 54.86, 53.70, 41.99, 40.10, 38.74, 32.14, 29.28, 25.05, 20.05 ppm; mass spectrum, calcd (M^+) *m/e* 174.1408, obsd 174.1413.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.68; H, 10.36.

Acknowledgment. We thank the National Cancer Institute (Grant CA-12115) for their financial support of this research.

Registry No. 3, 75725-33-6; **4**, 6675-72-5; **6**, 64489-06-1; **7**, 83134-44-5; **8**, 83134-45-6; **9**, 83134-46-7; **10**, 83134-47-8; **11**, 156-60-5; **12**, 83134-48-9; **13**, 1822-73-7; **14**, 83134-49-0; **15a**, 83134-50-3; **15b**, 83134-51-4; **16**, 73321-28-5; **17**, 83134-52-5; **18**, 53862-33-2; **19**, 20451-53-0; **20**, 83134-53-6; **21**, 83134-54-7; **22**, 5535-48-8; **23**, 73321-26-3; **24A**, 83134-55-8; **24B**, 83134-56-9; **24C**, 83198-37-2; **25**, 83134-57-0; **26**, 83134-58-1; **27**, 83134-59-2; **28**, 83151-98-8; **29**, 83134-60-5.

Dimethyl 1,1-Dicyanoethene-2,2-dicarboxylate, a New Electrophilic Olefin

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Dimethyl 1,1-dicyanoethene-2,2-dicarboxylate (DDED), a new electrophilic tetrasubstituted olefin, was synthesized via a Knoevenagel condensation. DDED spontaneously copolymerizes with electron-rich olefins such as styrene and *p*-methylstyrene. In the copolymerization, the bulky growing styryl radicals add to the dicyano-bearing carbon of DDED. Cyclobutane adducts are obtained in thermal reactions with styrene, *p*-methylstyrene, *p*-methoxystyrene, and vinyl ethers via a tetramethylene intermediate. Bond formation occurs at the diester end of DDED due to the greater stabilization provided by the dicyano group and the minimal steric requirements of the attacking methylene.

In our continuing study of the reactions of electron-poor and electron-rich olefins, we reported the spontaneous thermal copolymerization of dimethyl dicyanofumarate and styrenes.[1] This was a rare case of a (nonfluorinated) tetrasubstituted olefin capable of undergoing copolymerization. The lower energy barrier for cross-propagation of an electron-poor radical with an electron-rich monomer, and vice versa, may be enough to overcome the steric hindrance which usually prevents such reactions. Recently Vogl and co-workers[2] reported the copolymerization of dimethylmaleic anhydride and vinyl ethers, and we have described the copolymerization of bis(carbomethoxy)maleic anhydride and styrene.[3]

We postulate that spontaneous reactions between electrophilic and electron-rich olefins involve bond formation between the β-positions of the olefins, generating a tetramethylene intermediate which acts as a resonance hybrid of a zwitterion and a biradical structure.[4] If derived from polymerizable olefins, and depending on which character is predominant in the hybrid, the tetramethylene intermediate can initiate either cationic or anionic homo-

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[1] Hall, H. K., Jr.; Reineke, K. E.; Ried, J. H.; Sentman, R. C.; Miller, D. *J. Polym. Sci., Polym. Chem. Ed.* 1982, *20*, 361.

[2] Florianczyk, T.; Sullivan, C.; Janovic, Z.; Vogl, O. *Polym. Bull.* 1981, *5*, 521.

[3] Hall, H. K., Jr.; Sentman, R. C.; Nogues, P. *J. Org. Chem.*, in press.

[4] Hall, H. K., Jr.; Abdelkader, M. *J. Org. Chem.* 1981, *46*, 2948.

Table I. Copolymerizations of Dimethyl 1,1-Dicyanoethene-2,2-dicarboxylate with Electron-Rich Comonmers

comonomer	monomer ratio[a]	temp,[b] °C	solvent	% yield cyclobutane[c]	% yield polymer[d]	η_{inh},[e] dL g^{-1}
styrene	1:1	25	none	(21)	57	0.38
styrene	1:2	25	none	(trace)	48	0.23
styrene	1:1	25	MeCN	23 (85)	15	0.07
p-methylstyrene	1:1	25	none	(28)	39	0.32
p-methylstyrene	1:1	25	MeCN	56 (95)	trace	
p-methoxystyrene	1:1	25	none	(33)	*h*	
ethyl vinyl ether	1:1	25	none	97	0	
ethyl vinyl ether[f]	1:1	60	MeCN	0	30	0.25
isobutyl vinyl ether	1:1	25	none	95	0	
isobutyl vinyl ether	1:50	40[g]	none	0	0	

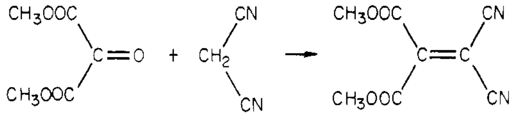
[a] DDED/comonomer. [b] Reaction time 18 h. [c] Yields in parentheses were determined by NMR (not isolated). [d] Based on DDED. [e] 0.5% solution in acetonitrile at 30 °C. [f] AIBN (0.25 mg) added. [g] Reaction time 36 h; attempt to initiate cationic polymerization. [h] Homopoly(*p*-methoxystyrene).

polymerization or radical-alternating copolymerization. The character of the tetramethylene intermediate is determined by the substituents on the terminals. Small molecule addition products such as cyclobutanes, 1-butenes, cyclohexanes, etc. also form in these reactions.

To extend these results, we have prepared and studied dimethyl 1,1-dicyanoethene-2,2-dicarboxylate (DDED). Like dimethyl dicyanofumarate, this olefin is quite electron deficient and might be another polymerizable tetrasubstituted olefin. In addition, the question of steric vs. electronic control of orientation could be addressed, since nitriles are better electron-withdrawing groups and esters are sterically more demanding.

Results

Synthesis. Dimethyl 1,1-dicyanoethene-2,2-dicarboxylate (DDED, 1) was prepared via a Knoevenagel condensation between dimethyl oxomalonate and malononitrile. A 5:1 ratio between ketone and malononitrile was found to optimize the yield of olefin; at a 1:1 ratio a second equivalent of malonitrile adds to form an unidentified propane.



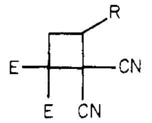
1 (DDED)

Cycloadditions and Copolymerizations. DDED spontaneously forms 1:1 copolymer when reacted in bulk with styrene or *p*-methylstyrene at room temperature. Yields of about 60% are obtained and the 1:1 copolymers are of reasonable molecular weight (Table I). Cyclobutane formation accompanies the polymerization. Addition of solvent effectively slows down the polymerization. At 25 °C cyclobutane formation proceeds, but the rate is very slow: no cyclobutane is formed after 8 h of reaction. High yields of cyclobutane can be obtained by heating to 70 °C. Some oligomerization also occurs under these conditions. No pyran cycloadducts resulting from [4 + 2] cycloadditions were observed. With *p*-methoxystyrene in bulk, DDED reacts to form cyclobutane and poly(*p*-methoxystyrene). The homopolymer possesses a low molecular weight and the yield is low.

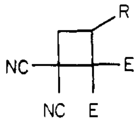
Ethyl or isobutyl vinyl ether gives only cyclobutane formation, and no spontaneous polymerizations occur. Addition of AIBN to these reactions in acetonitrile or benzene leads to formation of 1:1 copolymer.

Attempts to initiate homopolymerization of styrene and isobutyl vinyl ether with catalytic amounts of DDED failed.

Orientation of DDED in [2 + 2] Cycloadditions. Of the two possible cyclobutanes formed by the reaction of DDED with electron-rich olefins (**2a** and **2b**; E = $COOCH_3$) structure **2a** has been assigned on the basis of the following observations.



2a



2b

(a) In the mass spectrum of the cyclobutanes formed in the reaction of DDED with isobutyl or ethyl vinyl ether, or styrene, the metathesis products are observed. Only products of the form $[RCHC(CN)_2]^{+\cdot}$ are observed. Although these peaks are never large (10% for styrene), the complete absence of ions of the structure $[RCHC(COOCH_3)_2]^{+\cdot}$ in all cases is strong evidence for structure **2a**.

(b) The chemical shifts in the ^{13}C NMR spectra of the cyclobutanes do not agree with the values calculated by using the method of Levy, Lichter, and Nelson[5] (Table II). The spectra do, however, support structure **2a**. For example, for the cyclobutane from DDED and isobutyl vinyl ether, the signals for the carbonyl carbon appear at 166.9 and 165.9 ppm; the nitrile carbons appear at 112.6 and 110.8 ppm. The greater difference in chemical shift for the nitrile signals implies that these groups are closer to the point of dissymmetry as in structure **2a**.

(c) In the ^1H NMR spectra of several dimethyl (4-aryl)cyclobutane-1,1-dicarboxylates, one of the ester methyl groups is shifted upfield due to the interaction of the aromatic ring current. This shift is not seen in the spectra of the cyclobutanes obtained from DDED and several styrenes.

(d) Most acrylates carrying an additional electron-withdrawing group in the α-position form Diels-Alder adducts with electron-rich olefins, resulting in dihydro-2*H*-pyrans.[6] Thus, trimethyl ethenetricarboxylate, dimethyl cyanofumarate, dimethyl dicyanofumarate, and dimethyl 2-cyanoethene-1,1-dicarboxylate all form dihydro-2*H*-pyrans with vinyl ethers and either 3,4-dihydro-2*H*-pyrans or Wagner-Jauregg[7] adducts with styrene. Such adducts have not been observed in the reactions of DDED, implying that in the transition state the two ester groups do not face the electron-rich substituent;

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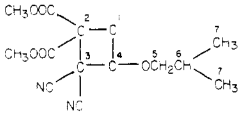
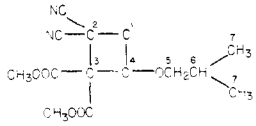
[5] Levy, G. C.; Lichter, R. L.; Nelson, G. L. In "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", Wiley: New York, 1980.

[6] Hall, H. K., Jr.; Rasoul, H. A. A.; Gillard, M.; Abdelkader, M.; Nogues, P.; Sentman, R. C. *Tetrahedron Lett.* **1982**, 603.

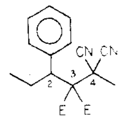
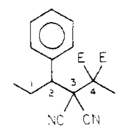
[7] Wagner-Jauregg, T. *Synthesis* **1980**, 769.

Table II. Calculated and Experimental ^{13}C Shifts (ppm) of Cyclobutanes from Reaction of DDED with Isobutylvinyl Ether

		carbon[b]									
compd	type	1 (t)	2 (s)	3 (s)	4 (d)	5 (t)	6 (d)	7 (q)	CN (2)	CO (2)	OCH_3 (2, 9)
	calcd[a]	42.6	56.1	32.4	73.3	77.0	27.1	20.6			
	calcd[a]	42.6	32.1	56.4	73.3	77.0	27.1	20.6			
	exptl	35.9	41.7	52.9	78.9	77.4	28.7	19.3	112.6, 110.8	166.9, 165.9	54.7, 54.0

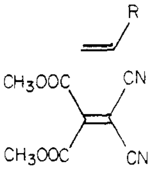
[a] For the method of calculation, see ref 5. [b] Carbon number followed by the multiplicity in parentheses.

Table III. Calculated and Experimental ^{13}C Shifts (ppm) of Alternating Copolymers of DDED and Styrene

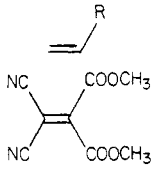
		carbon							
compd[c]	type	1	2	3	4	CO	CN	Ar	OCH_3
	calcd[a]	37.7	33.3	59.8	34.1				
	calcd[a]	37.7	33.4	35.8	58.1				
	exptl[b]	46.9	40.8	53.3	69.2	168.3, 167.9	114.9, 112.1	134.6, 132.6, 130.0	53.7

[a] For the method of calculation, see ref 5. [b] In $DCCl_3$, shifts relative to Me_4Si. [c] E = $COOCH_3$.

the orientation of the two olefins before reaction will be as in **a**, and not as in **b**.

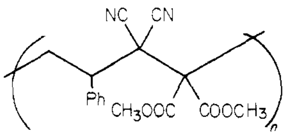


a

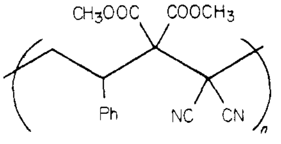


b

Orientation in the Copolymers. There are two possible structures for an alternating copolymer of DDED and styrene (**3a** or **3b**).



3a



3b

The ^1H NMR spectra of **3a** and **3b** are expected to be identical, so the ^{13}C NMR spectra were used to determine which one is formed. The results are tabulated in Table III. The extremely sharp lines suggest only one orientation in the polymer.

Calculations of expected chemical shifts for the backbone carbons via the "Additivity rules" of Levy, Lichter, and Nelson[5] give the values shown in Table III. The expected values from the two orientations are too close to be distinguished. In addition, comparison with the experimental values shows poor agreement between the observed and calculated shifts.

In order to determine the orientation, we prepared reference copolymers of unambiguous orientation from styrene and trisubstituted olefins with either two geminal carbomethoxy groups or two geminal cyano group. ^{13}NMR data and a representative calculation of expected chemical shifts for these copolymers are presented in Table IV. Note the lack of agreement between observed and expected shifts. Similar deviations are observed for the alternating copolymers of trisubstituted olefins with *p*-methoxystyrene.[8]

Examination of the data in Table IV shows that both polymers containing two ester groups in the γ-position (relative to the phenyl group) have a carbonyl signal at 168-169 ppm. Polymers containing two cyano groups in the γ-position produce a signal at 112–113 ppm. These signals arise from bis geminal groups that lie embedded on a sterically congested polymer backbone and could be expected to produce an absorption characteristic of that electronic/steric environment.

The observed carbonyl signals from DDED/styrene copolymer appear at 167.9 and 168.3 ppm. This correlates well with the carbonyl signals of the copolymers of the trisubstituted olefins with di-γ-carboxylates (Table V). The cyano groups of the DDED copolymer appear at 112.1 and 114.9 ppm. While the shift of 112.1 ppm does agree with those observed for the model copolymers, that at 114.9 ppm does not. On the basis of these results, the orientation in the copolymer has been assigned as in **3a**.

It should be mentioned that the above assignment is not unequivocal. It is assumed that the lack of agreement between calculated and experimental ^{13}C shifts is due to the extremely high degree of steric crowding and that the steric and electronic contributions of the second β sub-

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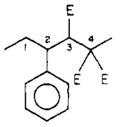
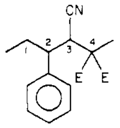
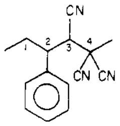
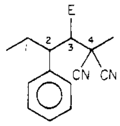
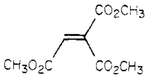
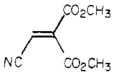
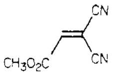
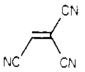
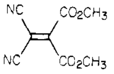
(8) Gillard, M.; Hall, H. K., Jr., private communication.

Table IV. ^{13}C NMR Spectral of Data (ppm)[a, b] of Copolymers of Styrene and Trisubstituted Electron-Poor Olefins

	carbon							
compd[c]	1	2	3	4	CO	OCH_3	CN	Ar
	41.1 (38.5)	39.8 (25.8)	42.5 (46.5)	59.0 (60.1)	171.8, 169.6	51.6, 51.3		127.4, 130.4, 126.5
	45.7 (38.5)	39.4 (25.8)	39.6 (34.5)	58.8 (60.1)	168.2, 168.8	52.4	117.6	128.4, 139.6
	44.6 (38.5)	35.9 (25.8)	36.5 (34.5)	40.3			112.6, 113.3	128.2
	43.8 (38.5)	36.3 (25.8)	56.7 (46.5)	37.4 (36.1)	168.6, 168.4	53.5	112.4, 112.8	134.5, 129.4

[a] Experimental value in $DCCl_3$, relative to Me_4Si. [b] Calculated value in parentheses. For the method of calculation, see ref 5. [c] E = $COOCH_3$.

Table V. ^{13}C NMR Shifts (ppm) of Carbonyl and Cyano Carbons in Copolymers of Styrene and Electron-Poor Olefins

electron-poor olefin	carbon	
	C=O	CN
	169.6, 168.6, 171.8, 171.4	
	168.2, 168.8	117.5
	168.6, 168.4	112.4, 112.8
		112.6, 113.3
	168.3, 167.9	114.9, 112.1

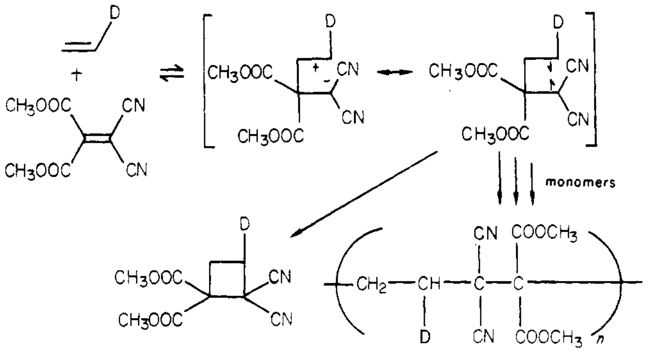
stituent are minimal. Models show these assumptions to be reasonable.

Discussion

DDED is another example, along with dimethyl dicyanofumarate[1], bis(carbomethoxy)maleic anhydride,[3] and dimethylmaleic anhydride,[2] of a tetrasubstituted electron-poor olefin capable of copolymerizing with electron-rich comonomers. The ability to design such olefins, with maximum electrostatic interactions and minimum steric hindrance, allows for the formation of polymers with a very high number of functional groups with a low degree of polymerization.

At the beginning of the paper the mechanism we have postulated for the reactions between electron-poor and electron-rich olefins has been described. DDED initially forms a charge-transfer complex with the electron-rich olefin, as witnessed by the intense colors formed. Bond formation leads then to a tetramethylene intermediate. The tetramethylene can collapse to a cyclobutane or initiate copolymerization.

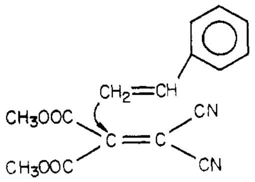
Scheme I[a]



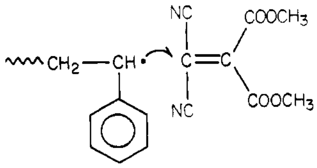
[a] D = donor group.

Two possible tetramethylene intermediates can be postulated: one with two cyano groups at the electrophilic end or one with two ester groups at that position. The cyclobutane structure confirms the structure of the tetramethylene in Scheme I. This tetramethylene is the electronically favored intermediate due to the greater stabilization provided by the cyano groups. The low steric requirement of the $CH_2=$ group permits bond formation at the sterically hindered carbon bearing two ester groups.

The spontaneous copolymerization is initiated by the tetramethylene hybrid, acting as a biradical. Attack on the cyano terminal can be ascribed to steric factors. The attack of the bulky styryl radical in the chain propagation reaction is more sterically demanding than the initial tetramethylene formation. Consequently, the polymerization is exclusively sterically controlled, while the tetramethylene formation is governed by electronic and resonance factors.



electronic control



steric control

The tetramethylene possesses more zwitterionic character in the reactions of DDED with vinyl ethers and *p*-methoxystyrene, as witnessed by the homopolymerization of the latter. The copolymer of DDED and ethyl vinyl ether is only obtained through addition of radical initiator.

Dilution of the reaction mixture favors cyclobutane formation over polymerization. The effect on concentration on the product ratio suggests a common intermediate for the two reaction paths.

Earlier[1] we suggested that the ability of dimethyl dicyanofumarate to copolymerize was derived from its planar structure, as shown by an X-ray crystallographic determination; this was suggested to minimize steric hindrance and permit maximum stabilization of the propagating radical. The present results cast some doubt on that idea. DDED is a liquid at room temperature, so we have been unable to establish its structure by X-ray crystallography. However, models indicate that the ester groups probably do not lie in the molecular plane.

In conclusion we can state that the donor substituent will determine the character of the tetramethylene intermediate when the acceptor moiety stays constant: phenyl and *p*-methylphenyl favor biradical character leading to both cyclobutane and copolymer, while alkoxy- and *p*-methoxyphenyl groups favor a zwitterionic tetramethylene. This supports our theory of the tetramethylene as a common intermediate for both the cyclobutane and polymer formation.

Experimental Section

Instrumentation. All melting points were determined in a Thomas-Hoover melting point apparatus and are uncorrected. Proton NMR spectra were recorded on Varian Model EM-360 spectrometer at 60 MHz and ^{13}C nuclear magnetic resonance spectra on a Brucker Model WM-250 Multinuclear FT spectrometer at 22.63 MHz. Infrared spectra were obtained with a Perkin-Elmer 337 grating infrared spectrophotometer. Mass spectra were determined on a Varian 311 A mass spectrometer with data analyzed with a Varian SS200. Elemental analyses were performed by the University of Arizona Analytical Center, Microlytics Inc., Skokie, IL, and Micanal, Tucson, AZ.

Chemicals. Solvents were reagent grade and were used as received or dried over calcium hydride. Malononitrile was distilled and stored cold in the dark. Styrenes and vinyl ethers were purchased from Aldrich and distilled from calcium hydride. Trimethyl ethenetricarboxylate,[9] dimethyl 2-cyanoethene-1,1-dicarboxylate,[10] dimethyl cyanofumarate,[9] and tricyanoethylene[11] were prepared as in the literature. Methyl glyoxylate was provided by Monsanto.

Monomer Synthesis. Dimethyl Oxomalonate. In a modification of the method of Pardo and Salomon,[12] 330.3 g (2.5 mol) dimethyl malonate was placed in 3-L three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. Bromine (850 g, 5 mol) was added dropwise rapidly, and the mixture was heated to 60 °C for 60 min, to 88 °C for 60 min, and cooled to 55 °C. Dry argon was bubbled through the reaction slurry overnight.

The reaction mixture was diluted with 500 mL of anhydrous methanol. Five portions of dry potassium acetate, the first 50 g in 150 mL of methanol and the second through the fifth (50 g each) in 100 mL of methanol, were added over a 4-h period and the mixture then refluxed overnight. After filtration to remove KBr, the methanol was removed under aspirator vacuum. Vacuum distillation [45–47 °C (0.05 torr)] of the impure acetyl bromomalonate gave 317 g (87%) dimethyl oxomalonate, NMR ($CDCl_3$) δ 4.0 (s).

Dimethyl 1,1-Dicyanoethene-2,2-dicarboxylate (DDED). Dimethyl oxomalonate (46.8 g, 0.32 mol), 5.28 g (0.08 mol) of malononitrile, 3.00 g of glacial acetic acid, 0.72 g of β-alanine, and 70 mL of toluene were heated at reflux with a Dean–Stark trap for 24 h. The toluene was removed under aspirator vacuum and the remaining solution vacuum distilled.

Unreacted oxomalonate was collected as the first fraction, 60% being recovered.

DDED was collected at 75–76 °C (0.05 torr). The pale green liquid was redistilled to give 13.6 g (0.07 mol, 82%) pure product: ^1H NMR ($CDCl_3$) δ 3.9 (s); ^{13}C NMR (Me_2 SO-d_6) δ 159.5 (CO), 109.4 (CN), 97.5, 93.8 (C=C), 54.5 (OCH_3); IR (neat, NaCl) 2995 (CH_3), 2230 (CN), 1740 (CO), 1610 (C=C). Anal. Calcd for $C_8H_6O_4N_2$: C, 50.01; H, 2.10; N, 14.58. Found: C, 49.57; H, 2.07; N, 14.45.

Methyl 2,2-Dicyanoacrylate (MDA). To methyl glyoxylate methyl hemiacetal (12.00 g, 0.1 mol), was added 5.68 g (0.04 mol) of P_2O_5 in five portions and the mixture stirred for 30 min. Distillation through a 30-cm fractional column under aspirator vacuum yielded pure methyl glyoxylate, 42 °C (20 torr).

Methyl glyoxylate (8.8 g, 0.1 mol), 3.3 g (0.05 mol) of malononitrile, 20 mL of benzene, 0.20 g of β-alanine, and 0.80 g glacial acetic acid were heated at reflux for 18 h in a Dean–Stark apparatus. Benzene and unreacted glyoxylate were removed under aspirator vacuum, and the remaining liquid was distilled under vacuum through a 30-cm fractionating column. MDA was collected at 53–55 °C (0.05 torr): yield 3.24 g (38%); NMR ($CDCl_3$) δ 7.2 (s, 1 H), 3.9 (s, 3 H); IR (NaCl, neat) 2995 (CH_3), 2225 (CN), 1740 (CO), 1600 (C=C) cm^{-1}. Anal. Calcd for $C_7H_7O_4N$: C, 49.71; H, 4.17; N, 8.28. Found: C, 49.56; H, 4.14; N, 8.30.

General Procedures for Bulk Reactions. The electron-poor comonomer (1 mmol) was weighed into a 10-mL Pyrex reaction tube and frozen at −78 °C. The electron-rich comonomer was added, by syringe, and the system was placed under vacuum for 3 min. The Pyrex tube was then sealed, and the reaction mixture was allowed to thaw and was stirred overnight at room temperature.

The reaction products were dissolved in chloroform, and polymers were precipitated with diethyl ether. After filtration, the polymers were redissolved in chloroform and precipitated with anhydrous methanol. All copolymers were found to have a C, H, and N content to within 0.5% of theory for 1:1 composition.

The ether from the original precipitation was removed by rotoevaporation. Any nonvolatile residue was dissolved in deuterated chloroform. If NMR indicated small molecules other than starting materials to be present, the solution was placed under 0.50-mm vacuum for several hours to remove unreacted styrene (or vinyl ether) and the product characterized by NMR.

General Procedures for Solution Reactions. The procedure followed was essentially as above except that 2 mL of dry acetonitrile or benzene was added and frozen prior to injection of the electron-rich olefin. Workup was as above.

If small molecules were desired from trisubstituted olefins, 0.01 g of diphenylpicrylhydrazyl (DPPH) was added to inhibit polymerization.

Cyclobutane Synthesis. Dimethyl 3-Isobutoxy-2,2-dicyanocyclobutane-1,1-dicarboxylate. DDED (0.194 g, 1 mmol) and 0.14 mL (1 mmol) of isobutyl vinyl ether were stirred in bulk at 25 °C overnight. Recrystallization from diethyl ether gave 98% (0.29 g) cyclobutane: mp 38–39 °C; NMR ($CDCl_3$) 4.8–4.5 (dd, J = 8, 8 Hz, 1 H), 3.9 (s, 6 H), 3.7–3.1 (m, 3 H), 2.9–2.7 (d, J = 8 Hz, 1 H), 2.2–1.5 (m, 1 H), 1.0–0.8 (d, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) 166.9 (s), 160.0 (s), 112.6 (s), 110.8 (s), 78.9 (d), 77.4 (t), 54.7 (q), 54.0 (q), 52.9 (s), 41.7 (s), 35.9 (t), 28.7 (d), 19.3 (q); mass spectrum, m/e 294, 238, 179, 150, 145, 113, 57 (BP). Anal. Calcd for $C_{14}H_{18}N_2O_5$: C, 57.13; H, 6.17; N, 9.52. Found: C, 56.89; H, 5.95; N, 9.61.

Dimethyl 3-Ethoxy-2,2-dicyanocyclobutane-1,1-dicarboxylate. DDED (0.194 g, 1 mmol) and 0.06 mL (1 mmol) ethyl vinyl ether were mixed and degassed. After being stirred for 18 h at 25 °C, the reaction mixture was dissolved in $CDCl_3$, transferred to 25 mL of diethyl ether, and placed at −60 °C for 3 h. Filtration isolated 0.305 g (97%) of cycloadduct: mp 63–64 °C; ^1H NMR ($CDCl_3$) δ 4.8–4.4 (dd, J = 18, 8 Hz, 1 H), 3.9 (s, 6 H), 4.0–3.3 (m, 3 H), 2.8 (d, J = 8 Hz, 1 H), 1.3 (t, J = 8 Hz, 3 H); mass spectrum, 266, 207, 179, 151, 147, 122, 133, 93, 72 (BP).

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Anal. Calcd for $C_{12}H_{14}N_2O_5$: C, 54.13; H, 5.30; N, 10.52. Found: C, 53.69; H, 5.19; N, 10.54.

Dimethyl 3-(*p*-Methoxyphenyl)-2,2-dicyanocyclobutane-1,1-dicarboxylate. DDED (0.194 g, 1 mmol) in 2 mL of acetonitrile and 0.12 mL (1 mmol) of *p*-methoxystyrene were stirred overnight at 25 °C. The solvent was removed under vacuum and subsequent recrystallization from diethyl ether/pentane produced 0.12 g (39%) of cyclobutane: mp 56–58 °C; NMR ($CDCl_3$) 7.4–6.8 (dd, 4 H), 4.7–4.3 (dd, $J = 8$, 11 Hz, 1 H), 3.9, 3.85, 3.80 (3 s, 9 H), 3.4–2.5 (m, AB, 2 H); mass spectrum, m/e 328, 208, 184, 134 (BP), 119, 113. Anal. Calcd for $C_{17}H_{16}N_2O_5$: C, 62.19; H, 4.91; N, 8.53. Found: C, 62.06; H, 4.86; N, 8.53.

Dimethyl 3-(*p*-Methylphenyl)-2,2-dicyanocyclobutane-1,1-dicarboxylate. DDED (0.194 g, 1 mmol) and 0.13 mL (1 mmol) of *p*-methylstyrene were stirred in 2 mL of acetonitrile overnight at 25 °C. Removal of the solvent left an orange oil, to which a vacuum was applied to remove excess styrene. The oil was dissolved in diethyl ether and placed at −60 °C, whereupon the solution separated into two layers. The ether was decanted off and the oil again placed under vacuum: yield 0.17 g (54%); NMR δ 7.2–6.9 (m, 4 H), 4.8–4.4 (m, 1 H), 3.9 (2 s, 6 H), 3.6–3.0 (m, 2 H), 2.4 (s, 3 H). Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 66.17; H, 5.14; N, 9.02.

Dimethyl 3-Phenyl-2,2-dicyanocyclobutane-1,1-dicarboxylate. DDED (0.194 g, 1 mmol) and 0.12 mL (1 mmol) of styrene were allowed to react in 2 mL of acetonitrile at 25 °C for 18 h. After removal of solvent and excess styrene under vacuum, recrystallization from ether/pentane gave 0.10 g (33%) of cyclobutane: mp 41–43 °C; NMR ($CDCl_3$) δ 7.2 (Ar, 5 H), 4.7 (m, 1 H), 3.8 (2 s, 6 H), 3.5–3.2 (m, 2 H); Mass spectrum, m/e 298 (molecular ion), calcd m/e 298, 178, 154, 72. Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.77; H, 4.71; N, 9.30.

Note Added in Proof: After this manuscript had been accepted, it came to our attention that the analogous compound diethyl 1,1-dicyanoethene-2,2-dicarboxylate had been synthesized on two occasions (Regan, T. H. *J. Org. Chem.* **1962**, *27*, 2236; Kociolek, K.; Lephawy, M. T. *Synthesis* **1977**, 778). The former utilized the same synthesis as ours, namely, the condensation of an oxomalonic ester with malononitrile.

Also, ethyl 1,1-dicyanoethene-2-carboxylate has been described (Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 295; Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 301.

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Registry No. 1, 82849-49-8; 1-styrene copolymer, 82849-60-3; 1-ethyl vinyl ether copolymer, 82849-61-4; 1-*p*-methylstyrene copolymer, 82849-62-5; MDA, 82849-50-1; dimethyl oxomalonate, 3298-40-6; dimethyl 3-ethoxy-2,2-dicyanocyclobutane-1,1-dicarboxylate, 82849-51-2; dimethyl 3-(*p*-methoxyphenyl)-2,2-dicyanocyclobutane-1,1-dicarboxylate, 82849-52-3; dimethyl 3-(*p*-methylphenyl)-2,2-dicyanocyclobutane-1,1-dicarboxylate, 82849-53-4; dimethyl 3-phenyl-2,2-dicyanocyclobutane-1,1-dicarboxylate, 82849-54-5; malononitrile, 109-77-3; styrene, 100-42-5; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4; ethyl vinyl ether, 109-92-2; isobutyl vinyl ether, 109-53-5; methyl glyoxylate, 922-68-9; dimethyl 3-isobutoxy-2,2-dicyano-1,1-dicarboxylate, 82849-59-0.

Notes

Vinyl Cations in Organic Synthesis. A New Route to Disubstituted Alkynes

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Disubstituted alkynes are usually prepared by elimination or substitution reactions.[1] However, these methods suffer structural and/or regiochemical limitations, which makes alternative procedures desirable. New interesting synthetic routes have been proposed, through vinyl selenoxides,[2] nitrimines,[3] β-oxo sulfones,[4] [(methylthio)methyl]lithium derivatives of carboxylic acids,[5] β-keto sulfones,[6] and diketones.[7] Starting materials and experimental procedures, however, are not always simple and involve, in any case, more than one step.

Our interest in the chemistry of vinyl cations[8] prompted us to investigate the feasibility of a new synthetic approach to disubstituted alkynes through such intermediates. Electrophilic additions of carbenium ions to triple bonds are well-known reactions: depending on the characteristics of the system and on the experimental conditions, different products can be obtained, deriving from addition and/or addition–elimination routes.[9] In particular, the latter can provide a simple way to transform 1-alkynes into disubstituted alkynes.

We report here the preliminary results of our study.

Results and Discussion

Phenylacetylene (**1**) was allowed to react in boiling dichloromethane with a series of diphenylmethyl sulfonic esters **2a–c**, prepared in situ by the reaction of di-

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