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Registry No. 1, 16282-16-9; 2, 21383-02-8; 3, 2371-23-5; 4, 38821-25-9; 5, 110797-71-2; β-cyclodextrin, 7585-39-9; deoxybenzoin, 451-40-1; 1,2-diphenylcyclobutan-1-ol, 63776-27-2; 1,2-diphenyl-4-methylcyclobutan-1-ol, 110797-72-3; 1,2-diphenyl-4-ethylcyclobutan-1-ol, 110797-73-4; 1,2-diphenyl-4-butylcyclobutan-1-ol, 110797-74-5.

Cycloaddition and Copolymerization of Methyl Tricyanoethylenecarboxylate with Electron-Rich Olefins

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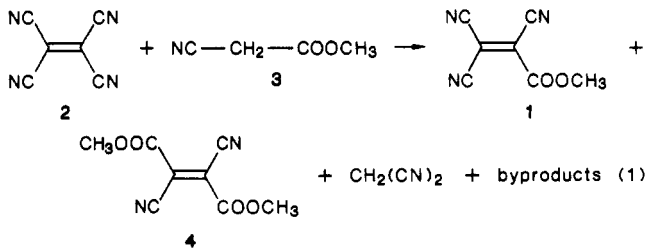
Methyl tricyanoethylenecarboxylate (1), an extremely electron-poor olefin, was synthesized by the exchange reaction of tetracyanoethylene and methyl cyanoacetate. The best yields for this reaction were obtained in the presence of pyridine. The cycloaddition reaction of 1 with electron-rich olefins such as *p*-methoxystyrene, *trans*-anethole, isobutyl vinyl ether, and ethyl *cis*-propenyl ether yielded cyclobutane and 3,4-dihydropyran adducts. The proposed mechanism involves a stepwise [2 + 2] reaction via a tetramethylene intermediate in competition with a [2 + 4] cycloaddition. The nature of the cycloadduct is determined by the orientation of the electrophilic olefin. Copolymerization of 1 with *p*-methoxystyrene under free-radical initiation gave an alternating copolymer.

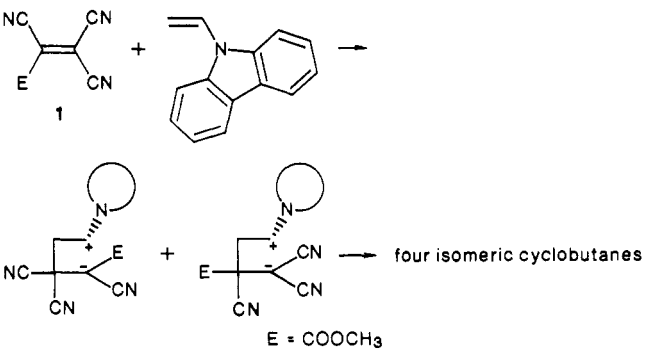
Methyl tricyanoethylenecarboxylate (1), an extremely electron-poor olefin, has been previously synthesized in this laboratory in 40% yield by the exchange reaction of TCNE (2) and methyl cyanoacetate (3) in acetic acid at 100 °C.[1]



Dimethyl dicyanofumarate (4) is formed if 1 undergoes a second exchange reaction with methyl cyanoacetate. The yields of this reaction vary a great deal from run to run and are rather low. In this study, the reaction will be studied in varying conditions in order to optimize the yield and reproducibility.

Methyl tricyanoethylenecarboxylate (1) has previously been compared to other tetrasubstituted electrophilic olefins in its reaction with *N*-vinylcarbazole.[1] In these reactions, the cyclobutane adducts are formed via a zwitterionic tetramethylene intermediate. Methyl tricyanoethylenecarboxylate was less electrophilic than TCNE, as could be deduced from cyclic voltammetry, from the λ_{max} value in the UV spectrum of the electron donor–acceptor (EDA) complex and from the rate of the cycloaddition reaction. Interestingly, the tetramethylene formation for this olefin with *N*-vinylcarbazole was not regiospecific, as witnessed by the formation of four isomeric cyclobutanes. This means that bond formation occurs at both the dicyano and the cyano carbomethoxy termini of the olefin, indicating that the electronic stabilization of the carbanion center by (CN, $COOCH_3$) is comparable to that by (CN, CN). The latter is preferred by a 60/40 ratio.

(1) Gotoh, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4920.



The nonregiospecificity of 1 is unique among all the electrophilic olefins we have studied over the years. Therefore, we will systematically investigate the cycloaddition and polymerization reaction of 1 with other electron-rich olefins, such as *p*-methoxystyrene, vinyl ethers, and anethole.

Results

Synthesis of Electrophilic Olefin 1. Methyl tricyanoethylenecarboxylate (1) was synthesized by a retro–Michael exchange reaction of tetracyanoethylene (TCNE, 2) and methyl cyanoacetate (3, eq 1). The reaction has to be carefully controlled, because if the conditions are too harsh, a second exchange reaction takes place and dimethyl dicyanofumarate is formed. The reaction was studied in both basic and acidic conditions. A catalyst is required, as no exchange occurred in a blank experiment.

Figure 1 shows the yield of 1 as a function of time under various conditions. The yields are determined by NMR spectroscopy. Basic catalysts such as triethylamine and pyridine lead to the highest yields, while acidic catalysts such as acetic acid and boron trifluoride are much less effective. The isolated yield of the reaction with pyridine as catalyst is much better than that of triethylamine due to easier isolation.

Cycloaddition Reactions. The cycloaddition between 1 and *p*-methoxystyrene, *trans*-anethole, isobutyl vinyl

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Table I. ^{1}H NMR Spectral Data of Cyclobutanes and Dihydropyrans

	chemical shift, δ					coupling const, Hz			
compd	H_1	H_2	H_3	CH_3 (ester)	CH_3 (ether)	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	yield, %
6	4.55	3.24	3.18	4.07	3.83	11.1	9.5	12.4	21
7	4.48	3.48	3.91	4.01	3.83	12.5	8.5	12.5	55
8	5.36	2.70	2.04	3.92	3.84	11.5	2.1	11.5	24
9	4.36	3.64		4.06	4.04	8.9			6.5
10	4.15	3.72		3.95	3.90	11.7			2.5
11	4.99	2.68		3.86	3.85	10.6			91
12	4.68	3.06	3.09	4.01		8.9	8.9	13.0	13.5
13	4.73	3.22	2.93	4.01		8.1	8.3	12.8	63
14	5.61	2.83	2.51	3.95		3.0	2.3	14.0	23.5
15	4.73		3.50	4.07	4.05		10.8		53
16	4.52		3.28	4.04	4.01		8.9		28
17	5.20	2.56		4.05	4.01	8.1			17

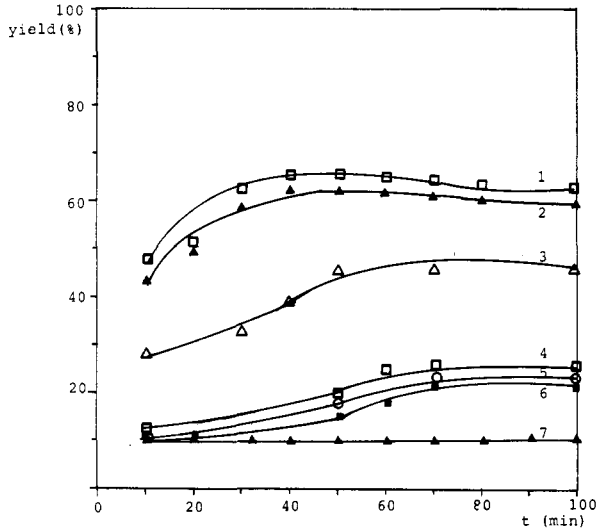
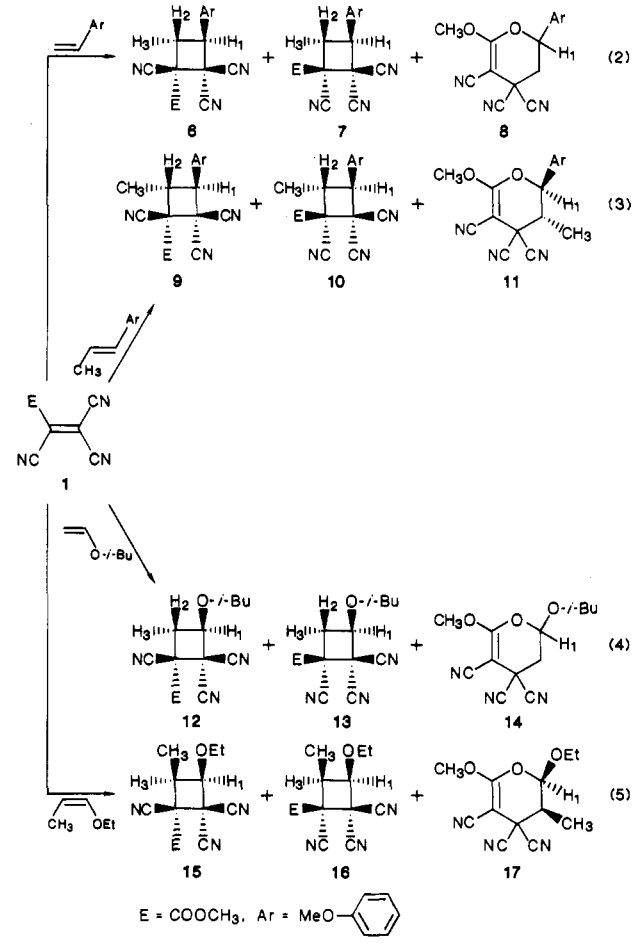


Figure 1. Yield of methyl tricyanoethylenecarboxylate (1) in the reaction of TCNE and methyl cyanoacetate in various conditions. (1) Triethylamine (0.1 mL)/tetrahydrofuran (10 mL) at 60 °C. (2) Pyridine (0.1 mL)/tetrahydrofuran (10 mL) at 60 °C. (3) Acetic acid at 100 °C. (4) Boron trifluoride etherate (3 mL)/nitromethane (10 mL) at 65 °C. (5) Methanesulfonic acid (3 mL)/nitromethane (10 mL) at 65 °C. (6) Trifluoroacetic acid at 65 °C. (7) Saturated solution of sodium acetate/acetic acid.

ether, and ethyl *cis*-propenyl ether to give both 3,4-dihydropyran and cyclobutane adducts (Scheme I). The reactions were complete within 4 h at 28 °C with 100% conversion of monomers to cycloadducts. No polymeric products were found. In reactions 2 and 4, cyclobutanes were separated from pyran adduct by liquid chromatography. The two cyclobutane isomers could not be separated in any of these reactions, but could be fully identified by NMR spectroscopy.

The cyclobutane adducts all display the nitrile absorption at ~2250 cm^{-1} and the ester carbonyl absorption at ~1745 cm^{-1} in the infrared spectrum. The structures of the two isomers obtained in each reaction were assigned on the basis of the chemical shifts of the ring protons (H_2 and H_3). All the NMR data are summarized in Table I. The proton cis to the ester group on the adjacent carbon will appear at lower field. The donor group, *p*-methoxyphenyl or alkoxy, also exerts a downfield shift on the cis proton. This is in agreement with the NMR data obtained for the *N*-vinylcarbazole adducts.[1] The coupling constants vary among the several adducts. If the donor group and the ester group are cis, the cyclobutane probably assumes the butterfly conformation, while in the trans form, a more planar conformation should be favored. All cyclobutane adducts have the carbon with the two nitrile groups next to the carbon carrying the donor substituent, as proven by mass spectrometry fragmentation.

Scheme I



The 3,4-dihydropyran adducts, obtained from a [2 + 4] cycloaddition, show a nitrile absorption at ~2205 cm^{-1} in the infrared and also a typical ketene acetal absorption at 1610 cm^{-1}. A characteristic signal at ~5.3 ppm in the NMR is also observed.[2]

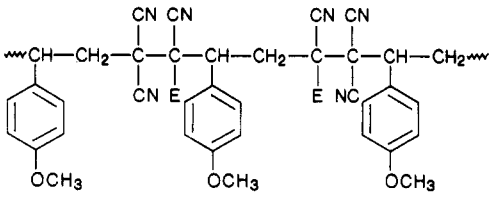
The reaction of methyl tricyanoethylenecarboxylate (1) with *p*-methoxystyrene (eq 2) yielded adducts 6–8 in roughly a 1:2:1 ratio. In the reaction of 1 with *trans*-anethole though, the [2 + 4] dihydropyran adduct is highly favored (>90%), with the two cyclobutane isomers formed in low yield. In the reaction of 1 with isobutyl vinyl ether, the cis cyclobutane (butoxy and ester groups cis) is again favored, but with ethyl *cis*-propenyl ether, the trans cyclobutane is formed in 53% yield. The data on the yield are included in Table I. In the reactions of 1 with

(2) Padias, A. B.; Hedrick, S. T.; Hall, H. K., Jr. *J. Org. Chem.* **1983**, *48*, 3787.

trans-anethole and ethyl *cis*-propenyl ether, no evidence was found for any isomerization of the substituents of the donor olefin. No polymer was ever observed in any of these spontaneous thermal reactions.

The effect of solvent polarity upon the rate of the reactions was studied with $CDCl_3$ and CD_3CN. When the solvent became more polar, reactions of 1 with *p*-methoxystyrene and *trans*-anethole were relatively unaffected in both reaction rates and the ratios between cyclobutanes to dihydropyran, but in the reactions of the vinyl ethers, the rates increased slightly.

Free-Radical Copolymerization of 1 with *p*-Methoxystyrene. With AIBN as a photoinitiator, 1 and *p*-methoxystyrene in $CHCl_3$, irradiated by UV light (2537 Å) overnight, gave a copolymer in 60% yield. After precipitation of this copolymer by ethyl ether and filtering, the filtrate showed no cyclobutane or pyran adducts by NMR. This copolymer had rather low molecular weight (M_n = 4000). Structure assignment was based on ^1H NMR, ^{13}C NMR, IR, and elemental analysis. In the ^{13}C NMR spectra, this copolymer showed several carbonyl signals at δ 159, 162, 163 and 164. This fact suggests more than one orientation of 1 in this polymer; the electrophilic olefin 1 is probably incorporated both ways.



Discussion

Cycloaddition. The tetrasubstituted olefin methyl tricyanoethylenecarboxylate (1) is highly electrophilic, as has been shown previously[1] and also in this work by the fast and efficient cycloaddition reactions with electron-rich olefins. It is, however, less electrophilic than TCNE, as would be expected.

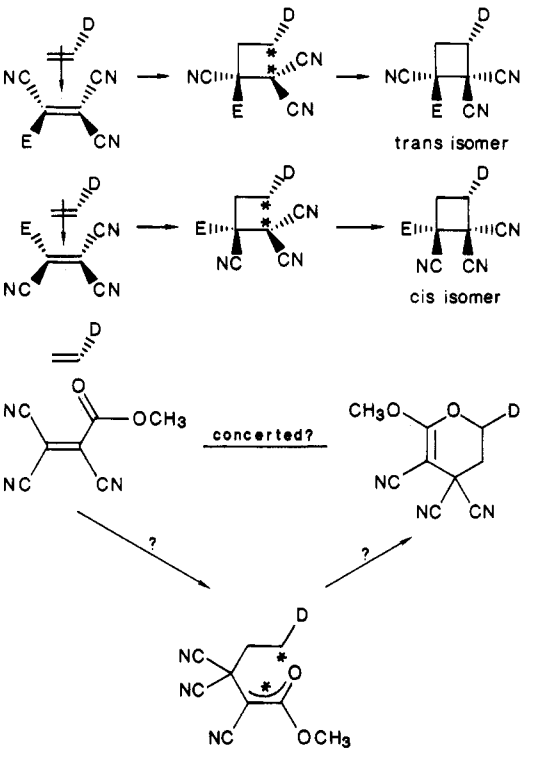
Two addition products are formed spontaneously in the reactions of 1 with donor olefins, cyclobutanes from a [2 + 2] cycloaddition, and 3,4-dihydropyrans from a [2 + 4] inverse electron-demand Diels–Alder reaction.

The cyclobutane adducts are formed in a stepwise fashion, in accordance with Woodward–Hoffmann rules. The intermediate is a tetramethylene intermediate. The nature of this intermediate is not quite clear at this point. The cycloaddition reaction of TCNE with *p*-methoxystyrene shows a tremendous solvent effect[3] and is assumed to proceed by a zwitterionic intermediate, although this intermediate has never been trapped.

On the other hand, the cycloaddition of methyl β,β-dicyanoacrylate with *p*-methoxystyrene is accompanied by spontaneous copolymerization, which indicates a diradical tetramethylene intermediate.[4] In the present study, no solvent effect is observed; the reactions proceed at basically the same rate in chloroform (nonpolar) and acetonitrile (polar), which would indicate a polar diradical intermediate in the case of *p*-methoxystyrene and anethole. However, no spontaneous copolymerization was observed.

For the reactions of 1 with vinyl ethers, the intermediate should be zwitterionic in analogy with previously studied reactions. Cycloadditions of TCNE with various vinyl ethers have been studied in great detail, and undoubtedly proceed by a zwitterionic tetramethylene intermediate.[5] The intermediate in the cycloadditions of methyl β,β-dicyanoacrylate and vinyl ethers can also be trapped by methanol, proving its zwitterionic character.[6]

Scheme II



* = radical or ionic, E = $COOCH_3$, D = donor substituent

The isomer ratio between cis and trans cyclobutane adducts (donor versus ester group) is completely determined by the configuration in the EDA complex. The two olefins slide over each other, and bond formation occurs to form the tetramethylene intermediate (Scheme II). In the case of *p*-methoxystyrene and isobutyl vinyl ether, the cis isomer is favored, because this conformation of the EDA complex allows maximum overlap of the orbitals. In the case of ethyl *cis*-propenyl ether, the trans isomer is formed preferentially; steric hindrance from the β-methyl group in the donor olefin probably favors the trans orientation in the EDA complex.

For the [2 + 4] cycloadduct, the 3,4-dihydropyran adduct, two mechanisms can be proposed: either a concerted reaction or a ring closure of the tetramethylene intermediate (Scheme II). The reactions of these electrophilic α,β-unsaturated esters with donor olefins have been studied in detail in earlier studies.[2,7] A transition from concerted to stepwise reactions was observed, depending on the electrophilicity of the olefins and the steric hindrance. The reactions of 1 with *trans*-anethole and ethyl *cis*-propenyl ether lead to only one isomer of the 3,4-dihydropyran adduct. A concerted reaction is stereospecific, but stereospecificity does not exclude a stepwise reaction.

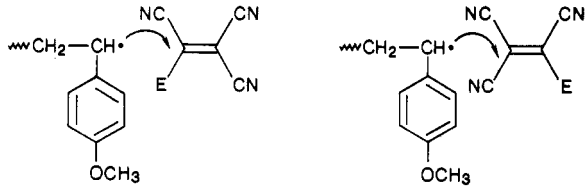
From these spontaneous cycloaddition reactions, we can conclude that the orientation of the two reacting olefins in the EDA complex completely determines the product. If the electrophilic olefin approaches the donor olefin with the two nitrile groups at the side of the donor substituent,

(3) Wiley, D. W., unpublished results. Ciganek, E.; Linn, W. J.; Webster, O. W. In *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Interscience: New York, 1970; p 423.
(4) Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.* **1987**, *52*, 4536.
(5) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.
(6) Padias, A. B., unpublished results.
(7) Hall, H. K., Jr.; Rasoul, H. A. A.; Gillard, M.; Abdelkader, M.; Nogues, P.; Sentman, R. C. *Tetrahedron Lett.* **1982**, *23*, 603.

then only cyclobutane adducts are formed, while if the ester group is at the same side of the donor group, only the 3,4-dihydropyran adduct is formed. No cyclobutane with the ester group adjacent to the donor group was ever isolated.

Copolymerization. In contrast to TCNE, methyl tricyanoethylenecarboxylate (1) does copolymerize with *p*-methoxystyrene if radical initiator is added. No spontaneous polymerization was ever observed.

The NMR spectra indicate that 1 is incorporated in both directions in the copolymer, which means that the growing *p*-methoxystyrene radical can attack either end of 1, as shown: I is the electronically favored mode of attack, due



electronic control I steric control II

to the greater stabilization provided by the cyano groups. II is sterically favored. The sterically favored attack (II) is consistent with the copolymerization of *p*-methoxystyrene with dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate, which gave the sterically controlled product.[8] Because the difference in electronic or steric factors is small between the two ends, neither one is favored in this particular copolymerization.

Experimental Section

Instrumentation. All melting points were obtained from a Thomas-Hoover capillary melting point apparatus. ^1H NMR and ^{13}C NMR spectra were taken on a Bruker WM 250 nuclear magnetic resonance spectrometer at 250 MHz. Infrared spectra were recorded on Perkin-Elmer 983 spectrometer. Number-average molecular weights were measured by size-exclusion chromatography on Du Pont ZORBAX PSM 60S, PSM 300S, and IBM GPC/SEC PORE type A columns calibrated with polystyrene, with chloroform as eluent. Elemental analyses were performed by MicAnal, Tucson, Az. Satisfactory analytical data (±0.4% for C, H, and N) were reported for 1, 6–8, 12, and 13.

Solvents. Solvents were dried over calcium hydride and distilled before use.

Reactants. Tetracyanoethylene (2) was purchased from Aldrich and was purified by two successive recrystallizations (chlorobenzene) and sublimations (120–130 °C, 0.5 mmHg) through an activated carbon layer. Mp: 198–200 °C.

p-Methoxystyrene was purchased from Aldrich, distilled from CaH_2, and stored under argon at −10 °C. Malononitrile and methyl cyanoacetate (Aldrich) were vacuum distilled before use.

Synthesis of Methyl Tricyanoethylenecarboxylate (1) with Pyridine as the Catalyst. TCNE (2; 2 g, 15.6 mmol) and methyl cyanoacetate (3; 0.78 g, 7.8 mmol) were dissolved in 10 mL of tetrahydrofuran at 60 °C. After 5 min, pyridine (0.1 mL) was added. The mixture was stirred for 30 min at 60 °C. Solvent and pyridine were removed under vacuum below room temperature. The residue was distilled with a Kugelrohr apparatus. The distillate between 75 and 120 °C (0.1 Torr) contained 1–3 and some black byproducts. This distillate was dissolved in 500 mL of $CHCl_3$ and then passed through enough activated carbon to remove the black color. The mixture was then separated by semipreparative HPLC (cyano RP packing, mobile phase $CHCl_3$/*n*-hexane, 1/1, v/v). Yield: 0.76 g (62%). Mp: 89.5–90.5 °C. IR (KBr): 2215 (CN), 1755 (CO stretch), 1680, 1600 (C=C stretch), 1315–1242 (ester stretch). ^1H NMR ($CDCl_3$): δ 4.07 (s).

Reaction of 1 with *p*-Methoxystyrene. Compound 1 (0.47 g, 2.974 mmol), *p*-methoxystyrene (0.090 g, 2.974 mmol), and $CHCl_3$ (1.5 mL) were mixed at 27 °C. A deep blue color formed. After 40 min, the color turned to brown. The mixture was left for 4 h at 27 °C. Complete reaction was confirmed by NMR. After 4 h, the solvent was removed under aspirator vacuum. The residue was separated as cyclobutanes 6 and 7 and dihydropyran 8 by reverse-phase liquid chromatography (cyano RP packing; $CHCl_3$/*n*-hexane, 1/1, as mobile phase).

Methyl 1-(*p*-methoxyphenyl)-2,2,3-tricyanocyclobutane-3-carboxylate (6 and 7). Mp: 99–102 °C. IR (KBr): 2260 (CN), 1745 (C–O stretch) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 162.2, 160.7 (CO), 114.6, 114.1, 111.2 (CN), 77.4, 77.0, 45.2, 45.9, 46.6, 31.4, 33.0. MS, *m/e* 295 (M^+), 197 (M^+ − $CH(CN)(COOCH_3)$), 184 ($CH_3OPhCHC(CN)(COOCH_3)^+$), 175 ($M^+$ − CH_3OPhCH), 134 ($CH_3OPhCHCH_2^+$), 120 (CH_3OPhCH^+).

2-(*p*-Methoxyphenyl)-4,4,5-tricyano-6-methoxy-3,4-dihydro-2*H*-pyran (8). Mp: 54–55 °C. IR (KBr): 2205 (CN), 1610 (C=C). ^{13}C NMR ($CDCl_3$): δ 167.8 (=CO_2), 112.5, 114.2 (CN), 78, 77, 67, 56, 55.

Reaction of 1 with *trans*-Anethole. Compound 1 (0.03 g, 0.189 mmol), *trans*-anethole (0.028 g, 0.189 mmol), and $CDCl_3$ (1.5 mL) were reacted in a Y tube for 4 h at 27 °C. A deep purple color formed, and after 3 h, the color turned to brown. The mixture was identified by ^1H NMR and ^{13}C NMR (see Table I), but the products were not isolated.

Reaction of 1 with Isobutyl Vinyl Ether. Compound 1 (0.042 g, 0.26 mmol), isobutyl vinyl ether (0.026 g, 0.26 mmol), and $CDCl_3$ (1.5 mL) were mixed in a Y tube at 27 °C. The mixture was then left for 4 h at 27 °C. The cyclobutanes and pyran were separated with HPLC and identified by ^1H NMR (see Table I), ^{13}C NMR, and IR.

Methyl 1-Isobutoxy-2,2,3-tricyanocyclobutane-3-carboxylate (12 and 13) (oil). IR (neat): 2261 (CN), 1748 (C=O) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 161.1, 163.7 (CO), 113, 110, 109, 108.4 (CN), 77.1, 43.3, 43.1, 41.7, 36. MS, *m/e* 261 (M^+), 205 (M^+ − isobutyl + 1), 150 (isobutyl ($OCHC(CN)CO_2CH_3$), 112 (M^+ − 150 + 1), 57 (isobutyl).

2-Isobutoxy-4,4,5-tricyano-6-methoxy-3,4-dihydro-2*H*-pyran (14). Mp: 103.5–104 °C. IR (KBr): 2210 (C), 1623 (C=C) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 165.3 (=CO_2), 127, 125, 114.2, 114.1, 113 (CN), 25.3.

Reaction of 1 with Ethyl *cis*-Propenyl Ether. Compound 1 (0.04 g, 0.253 mmol), propenyl ethyl ether (0.021 g, 0.253 mmol), and $CDCl_3$ (1.5 mL) were mixed in a Y tube at 27 °C. After 4 h, the mixture was identified by ^1H NMR (see Table I).

Copolymerization of 1 with *p*-Methoxystyrene. A quartz tube, containing a mixture of 1 (0.18 g, 1.153 mmol), AIBN (0.237 g, 0.023 mmol), and $CHCl_3$ (10 mL), was degassed twice, and after reintroduction of argon, *p*-methoxystyrene (0.154 g, 1.153 mmol) was injected. The mixture was irradiated with UV light (2537 Å) for 18 h at 0 °C. The polymer was twice precipitated into ethyl ether and dried under vacuum. The molecular weight determined by size exclusion was 50 000. NMR ($CDCl_3$): δ 6.2–7.1 (br, 4 H), 3.6–4.1 (br, 6 H), 1.6–3.2 (br, 4 H). Anal. Calcd for $C_{16}H_{13}O_3H_3$: C, 65.08; H, 4.40; N, 14.23. Found: C, 65.81; H, 4.39; N, 14.71.

Acknowledgment. We are deeply indebted to the National Science Foundation (Grant DMR-84-00970) for generous support of this research.

(8) Hall, H. K., Jr.; Sentman, R. C. *J. Org. Chem.* **1982**, *47*, 4572.