products, and all runs that were checked showed that these compounds accounted for all the initial diazonium salt.

For runs with excess BF_3, a solution of the diazonium salt was prepared as above and placed in a bubble tube equipped with stopcocks at both ends. BF_3 was bubbled through the tube for several minutes, and then the stopcocks were closed, sealing the tube. At the end of 10 days, the tube was opened and 1 ml of the solution was pipetted into water to hydrolyze the BF_3. The H_3BO_3 thus produced was titrated by standard methods. The rest of the solution was analyzed for products as above. In the runs with excess Br_2, Br_2 concentration was determined by $Na_2S_2O_3$ titration of I_2 liberated from KI.

p-tert-Butylhalobenzenes which were used as standards to calibrate the glc were prepared by reaction of the appropriate halobenzene with *tert*-butyl chloride in the presence of $FeCl_3$. The literature procedure for chlorobenzene[8] was also used for fluoro- and bromobenzene.

References and Notes

(1) Supported in part by research grants from the National Institutes of Health and the National Science Foundation.
(2) C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Amer. Chem. Soc.*, **97**, 783 (1975).
(3) C. G. Swain, J. E. Sheats, D. G. Gorenstein, and K. G. Harbison, *J. Amer. Chem. Soc.*, **97**, 791 (1975).
(4) C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Amer. Chem. Soc.*, **97**, 796 (1975).
(5) G. Balz and G. Schiemann, *Chem. Ber.*, **60B**, 1186 (1927); ref 41b of ref 2; G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, **26**, 2053 (1961).
(6) K. L. Nelson and H. C. Brown, *J. Amer. Chem. Soc.*, **73**, 5605 (1951).
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Reactions of the Zwitterions from Trisubstituted Electron-Deficient Ethylenes and Electron-Rich Olefins

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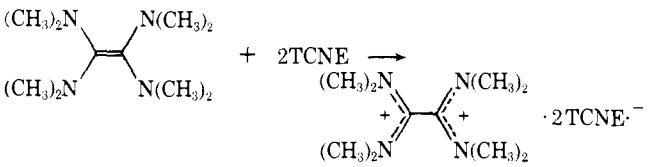
Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721. *Received May 2, 1974*

Abstract: Reactions of a series of electrophilic trisubstituted olefins (**1–4**) with a series of electron-rich olefins (**5–10**) were studied. The reactivities increased sharply with the degree of electrophilic and nucleophilic character, respectively; however, steric effects of β substituents prevented a 1:1 correspondence. The kinetically favored products were cyclobutanes in almost all cases. In polar solvents or on heating, they isomerized to olefinic adducts *via* hydrogen shift or underwent cycloreversion. All this behavior could be understood in the context of a zwitterionic intermediates, as described by earlier investigators in related systems. However, formation of 2-*N,N*-dimethylamino-1,1-dicyanoethylene (**11**) from reactions of tricyanoethylene with *N,N*-dimethylvinyl- or -isobutenylamines appeared to occur by a concerted cleavage of an unstable cyclobutane. Facile olefin metathesis occurs in the region between cyclobutane formation and direct electron transfer.

Reactions of electrophilic olefins with nucleophilic olefins comprise an interesting and versatile chapter of organic chemistry. Electrophilic olefins containing a single electron-withdrawing group (acrylonitrile, methyl acrylate) or two such substituents in the 1,2 positions (fumaronitrile, diethyl fumarate) require elevated temperatures to bring about reaction with even the extremely nucleophilic aliphatic enamines, although enamines containing β hydrogens react under milder conditions.[1]

At the other extreme of electrophilic character, tetracyanoethylene reacts readily at room temperature with a wide variety of moderately electron-rich olefins.[2] Other extremely electrophilic tetrasubstituted ethylenes including 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene[3] and the isomeric 1,2-bis(trifluoromethyl)-1,2-dicyanoethylenes[2] behave similarly. With aggressive electrophiles such as these, the activating substituent in the electron-rich partner can be nonbasic nitrogen (*N*-vinylamides, *N*-vinylsulfonamides, *N*-vinylcarbazole), oxygen (vinyl ethers), sulfur (vinyl sulfides), or carbon (*p*-methoxystyrene, cyclopropylethylene[2b,c]). Under very mild conditions, enamines reacted with the very active TCNE to give 1,1,2-tricyano-3-alkyl-4-*N,N*-dialkylaminobutadienes.[4] Wiberg[5] showed that, in the extreme case, tetrakis(dimethylamino)ethylene reacted with tetracyanoethylene in a redox manner:

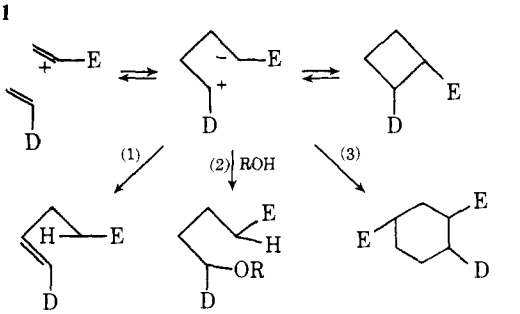


With the exception of this last unusual reaction, all the reactions cited involved formation of a zwitterion intermediate in the rate-determining step. Detailed mechanistic studies on the cycloaddition of TCNE to vinyl ether have been carried out by Huisgen and his collaborators.[6] Large solvent effects on the rate constant were observed. Particularly in the more polar solvents, the zwitterion was sufficiently long-lived to permit conformational rotation and loss of stereochemistry. A study[7] of the effect of pressure on these reactions lent further support to the presence of a zwitterion intermediate.

In the reactions of para-substituted styrenes with TCNE, the ρ value was -7.2,[8] and enormous solvent effects on the rate constants were observed. All these observations strongly point toward rate-determining zwitterion formation in these reactions also.

The zwitterion proceeds to products in a variety of ways (Scheme I). The cyclobutane is usually the kinetically favored product. However, owing to ring strain and substitu-

Scheme I

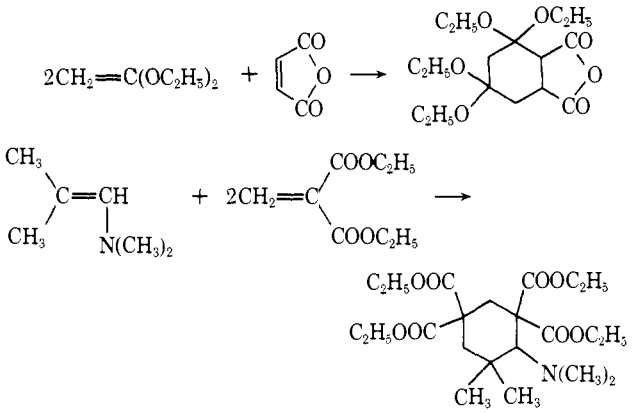


ent effects, it is thermodynamically unstable[1,2,6] and may revert to zwitterion.

The rate of reversion to zwitterion is greatly increased by heat and by strongly polar solvents which can solvate the zwitterion. This ion can then proceed to more thermodynamically favored products. If β hydrogens are present, hydrogen shift in the zwitterion usually leads to open-chain linear unsaturated adducts[9,10] (reaction 1). In protolytic solvents, the zwitterion may be trapped (reaction 2).

Finally, structurally stabilized zwitterions can add another molecule of either the electron-rich or the electron-poor olefin with eventual formation of cyclohexane derivatives (reaction 3). MacElvain and Cohen[11] have observed reaction with the former and Brannock and his colleagues[9] reaction with the latter (Scheme II). Charge-transfer com-

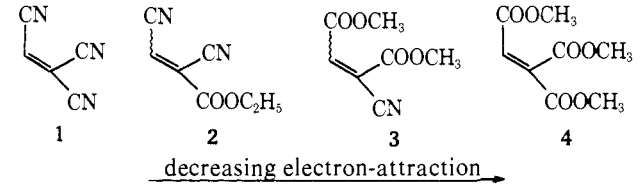
Scheme II



plexes undoubtedly form during many of these reactions as evidenced by transient intense colors of the reaction solutions. Whether or not they lie directly on the reaction path has not been definitely established.

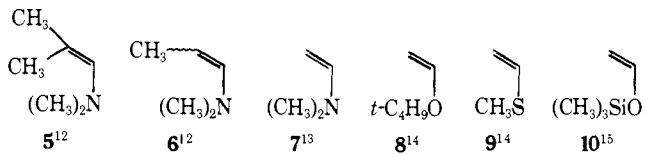
The intermediate range of electrophilic behavior between that of acrylonitrile and methyl acrylate, on the one hand, and TCNE and its relatives, on the other, has been little explored. Information about rate and products would be valuable in order to expand the range of applicability of the concept of the zwitterion intermediates. The only example of cycloaddition involving a 1,1-disubstituted electrophilic olefin which we have found is the case of diethyl methylenemalonate.[9] Among trisubstituted electrophilic olefins, tricyanoethylene has been reported to react with two vinyl ethers.[2a]

Because the trisubstituted olefins do not homopolymerize, and a graded series is readily accessible, the compounds **1–4** were chosen as reactive partners for electron-rich olefins.



decreasing electron-attraction →

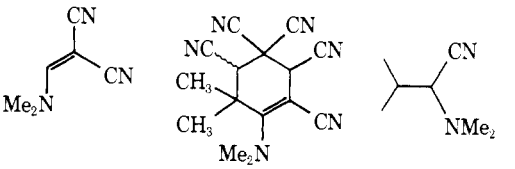
For a correspondingly graded series of electron-rich olefins, compounds **5–10** were selected. They are listed approximately in the order of decreasing electron density.



decreasing electron-donation →

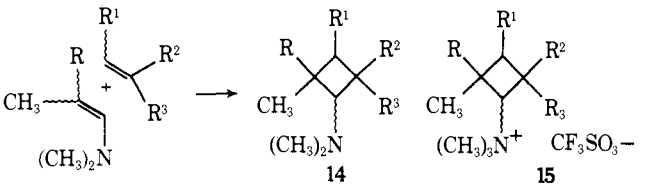
Results

***N,N*-Dimethylisobutenylamine.** The reaction of equimolecular amounts of *N,N*-dimethylisobutenylamine and tricyanoethylene at 0° in ether was almost explosive. We were able to isolate 1,1-dicyano-2-*N,N*-dimethylaminoethylene (**11**, traces), 1-*N,N*-dimethylamino-2,3,4,4,5-pentacyano-6,6-dimethylcyclohex-1-ene (**12**, 6% yield), and 1-*N,N*-dimethylamino-1-cyano-2-methylpropane (**13**, 21% yield).



When mixed at −60° in toluene, equivalent amounts of reactant gave a red solution. After 2 days, no change having been observed, the solution was allowed to come to room temperature. Crude **12** precipitated from the reaction mixture at room temperature and was isolated in purity in 32% yield; **13** and **11** (traces) were isolated as well.

The other three, less electron-demanding trisubstituted olefins gave cyclobutane derivatives. Reacted with 3 equiv of *N,N*-dimethylisobutenylamine in ether at −55°, ethyl 2,3-dicyanoacrylate (**2**) gave an intermediate blue oil and then a white precipitate. The crystals were filtered cold and consisted mainly of the cyclobutane **14a**. At room temperature, this cycloadduct decomposed; however, it could be trapped as the stable quaternary ammonium salt **15a** by methylation with methyl triflate at −70°.



a, R = CH_3; R^1 = R^2 = CN; R^3 = $COOC_2H_5$
b, R = CH_3; R^1 = R^2 = $COOCH_3$; R^3 = CN
c, R = CH_3; R^1 = R^2 = R^3 = $COOCH_3$
d, R = H; R^1 = R^2 = R^3 = $COOCH_3$

With 2 equiv of *N,N*-dimethylisobutenylamine at −15° in ether, dimethyl 1-cyanoethylene-1,2-dicarboxylate gave cyclobutane **14b** isolated in 78% yield. An nmr study showed that reacting 1.2 equiv of enamine with the electron-poor olefin at −15° still gave only the desired cycloadduct, but that a 1:1 mol ratio at 28° gave less clean results. A second product was formed in these reactions, but has not been finally identified. Methylation with methyl triflate at −70° gave quaternary salt **15b** in 65% yield as a stable derivative.

N,N-Dimethylisobutenylamine reacted smoothly at room temperature in ether with trimethyl ethylenetricarboxylate to give after 1 day as sole product cyclobutane **14c**, isolated in quantitative yield. From the melting range (44–51°) and the nmr spectrum, it appeared to be a mixture of isomers.

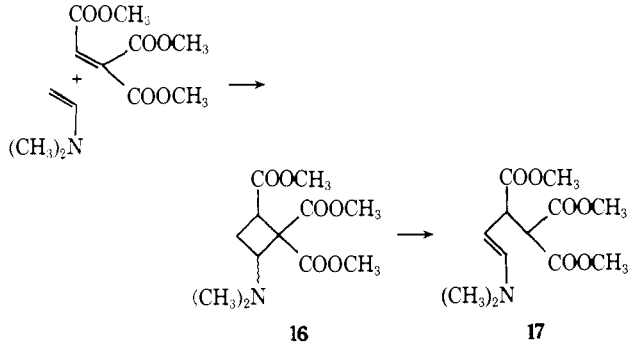
Heating cyclobutane **14c** at 155–170° under vacuum (attempted distillation) caused cycloreversion to starting materials. Methylation at −70° gave salt **15c** in 85% yield.

***N,N*-Dimethylpropenylamine.** The cycloaddition of *N,N*-dimethylpropenylamine to trimethyl ethylenetricarboxylate was studied briefly. Keeping the reaction mixture for several days at −78° allowed isolation of a precipitate which partly melted at room temperature. Its nmr spectrum revealed vinylic absorptions. However, quaternization of the reaction mixture maintained at −78° gave the quaternary

salt **15d** of the cyclobutene cycloadduct **14d** in 29% yield.

***N,N*-Dimethylvinylamine.** *N,N*-Dimethylvinylamine interacted instantly with tricyanoethylene in toluene at −55° to give a dark color. After 1 day at that temperature, the reaction mixture was allowed to come to room temperature. Evaporation of the solvent and extraction with ether gave 1,1-dicyano-2-*N,N*-dimethylaminoethylene (**11**, 24% yield).

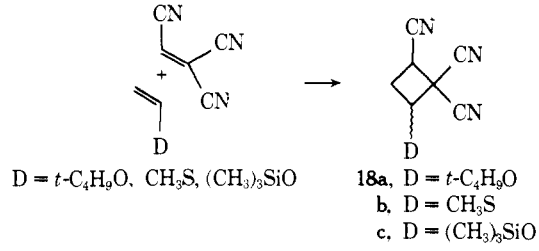
N,N-Dimethylvinylamine reacted with trimethyl ethylenetricarboxylate at −55° in ether to give after 1 hr a white precipitate which could be isolated by filtration. At room temperature, this precipitate became a slightly yellow liquid which on standing in the refrigerator gave a slightly yellow solid (isolated in 88% yield). This product was crude trimethyl 1-*N,N*-dimethylamino-*trans*-1-butene-3,4,4-tricarboxylate (**17**). From these observations, it is reasonable to assume that the initial white unstable solid was again the intermediate cyclobutane **16** formed by cycloaddition, and which decomposed at room temperature.



16 **17**

Attempted alkylation of **16** at −70° did not succeed; from the nmr spectrum it appeared that alkylation of **17** had taken place.

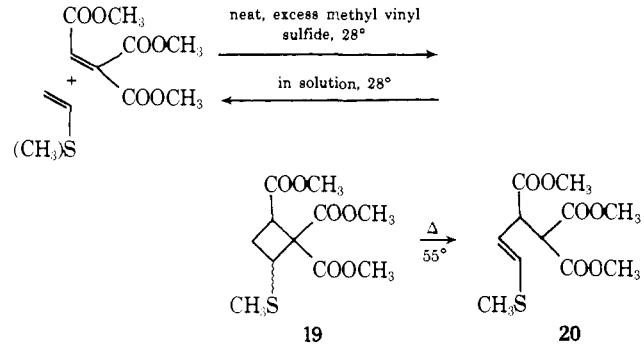
***tert*-Butyl Vinyl Ether.** Reacted with *tert*-butyl vinyl ether in benzene at room temperature, tricyanoethylene gave instant heat evolution and an orange color. An nmr spectrum taken after 1 day showed only two isomeric cyclobutanes (**18a**). Evaporation and crystallization gave the product in 68% yield. This is consistent with the results of previous investigators.[2a,16]



D = *t*-C_4H_9O, CH_3S, $(CH_3)_3SiO$ **18a**, D = *t*-C_4H_9O; **b**, D = CH_3S; **c**, D = $(CH_3)_3SiO$

Methyl Vinyl Sulfide. When equivalent amounts of methyl vinyl sulfide and tricyanoethylene were mixed in benzene at room temperature, the solution instantly became dark and warm. An nmr spectrum taken after 3 hr showed only the isomeric cyclobutanes **18b**. Crystallization from ether gave a mixture of the two isomers in 73% yield. Recrystallization gave each isomer in purity.

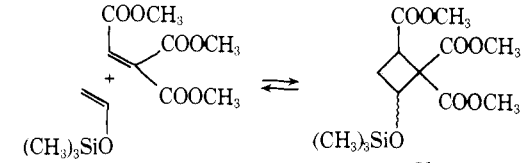
Two equivalents of methyl vinyl sulfide reacted with 1 equiv of trimethyl ethylenetricarboxylate in 3 days at room temperature to give cyclobutane **19** (>95% conversion by nmr, isolated in 47% yield). Left for 1 day in deuteriochloroform, **19** underwent cycloreversion to starting materials to the extent of 30%; that ratio remained constant. On warming to 55°, moreover, **19** underwent ring opening with hydrogen shift to give the linear unsaturated isomer **20**.



19 **20**

Trimethylsilyl Vinyl Ether. Trimethylsilyl vinyl ether reacted at room temperature with tricyanoethylene in benzene or in THF.[16] An nmr spectrum taken after 4 hr of reaction showed only the isomeric cyclobutanes in ratio 57:43. Removal of solvent under vacuum allowed the cycloadduct **18c** to be isolated quantitatively.

When the reaction of trimethylsilyl vinyl ether with trimethyl ethylenetricarboxylate was carried out at 47° with 2 equiv of the former, only an approximately 1:1 copolymer was obtained. Under the same conditions, but in the presence of *tert*-butylhydroquinone, cycloadduct **21** was obtained quantitatively after 15 days. Attempts to recrystallize **21** failed.



21

Heating cyclobutane **21** at 180° under vacuum (attempted distillation) caused cycloreversion to trimethylsilyl vinyl ether and trimethyl ethylenetricarboxylate.

Charge-Transfer Complexes. In many of the reactions cited above, transient deep colors were observed. These have been observed by previous workers in the field and are ascribed to charge-transfer complexes.

The dark colors of reaction mixtures involving tricyanoethylene and enamines are not transient, however; they probably are caused by oligomerization of the olefin in the basic reaction medium, forming conjugated C=N structures from the CN groups.

Discussion

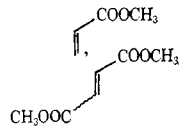
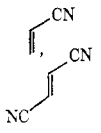
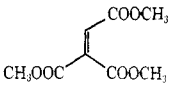
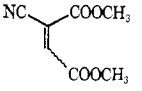
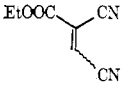
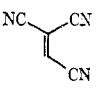
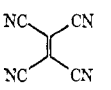
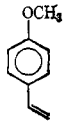
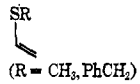
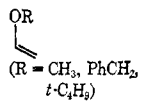
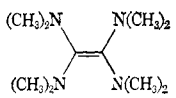
As described above, our interest centered on the reactivity of electrophilic trisubstituted olefins with nucleophilic olefins and the nature of the products. The results can best be presented with the aid of Chart I, a "Periodic Table for Cycloadditions," where the nucleophilic and electrophilic olefins have been listed in expected orders of increasing electron excess and deficiency, respectively.

Reactivity. Electronic effects on the rates of the reactions were very pronounced. As the trisubstituted olefin became more electronegative (to the right in Chart I) and the monosubstituted olefin became more electron rich (downward), the rates increased strongly, and the required reaction temperatures became lower. This agrees with the rate-determining formation of the zwitterion.

When β substituents are present in either component, the order of electron deficiency or excess cannot be taken as the order of reactivity because of steric effects.[6d]

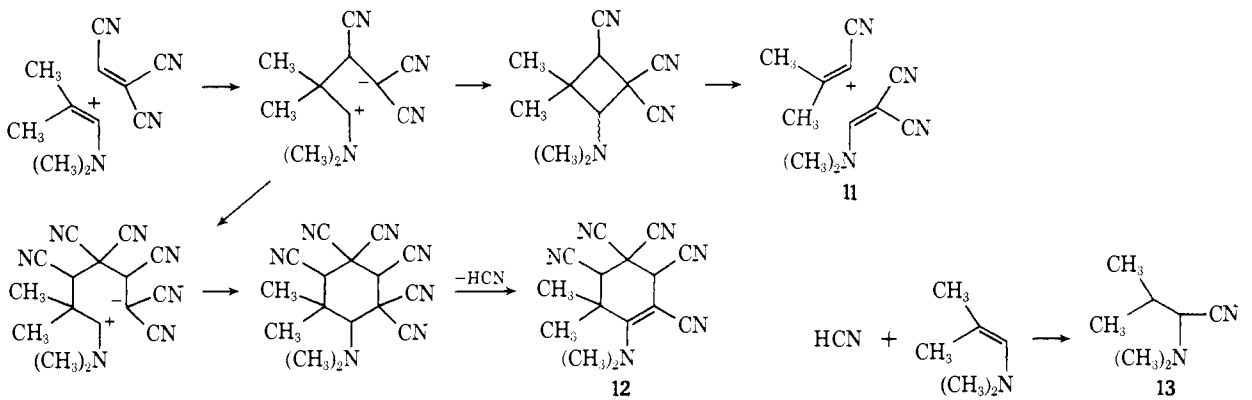
Thus with trimethyl ethylenetricarboxylate, the following order of reactivity was noted: *N,N*-dimethylvinylamine, immediate reaction at −55°; *N,N*-dimethylpropenylamine, reaction complete in a few minutes at −55° (transient orange color); *N,N*-dimethylisobutenylamine, reaction complete in 1 day at 28°.

Chart I. Products from the Reaction of Electrophilic and Nucleophilic Olefins[a]

							
				Spontaneous copolymerization[24]			Cyclobutane,[2] hours, rt, THF
			Copolymer, 47°, neat; cyclobutane, 15 days, 47°, neat			Cyclobutane 4 hr, rt, C_6H_6	
			Cyclobutane, 3 days, rt, neat; open chain, 55°; reversion, rt, $CHCl_3$	Cyclobutane and open chain, 1 hr, rt, neat		Cyclobutane, 3 hr, rt, C_6H_6	Cyclobutane,[2] hours, rt, THF
						Cyclobutane,[2] hours, rt, C_6H_6, THF	Cyclobutane,[2] hours, rt, THF
			Cyclobutane, −78°, ether; open chain, rt, ether or neat			Metathesis, toluene, −55°	
	Cyclobutane,[1] hours, rt, or reflux, CH_3CN	Cyclobutane,[1] hours, rt, or reflux, CH_3CN	Cyclobutane, minutes, −55°, ether; open chain, rt				
	Cyclobutane,[1] 2 hr, 170°, neat	Cyclobutane,[1] 2 hr, 170°, neat	Cyclobutane, 1 day, rt, ether	Cyclobutane, minutes, −15°, ether	Cyclobutane, minutes, −78°, ether	Metathesis and 2:1 adduct, −60°, toluene	
							Redox[5]

[a] rt means room temperature.

Scheme III



Products. Given a degree of electronic imbalance in the reagents sufficient to bring about reaction, cyclobutane derivatives are the generally expected products. Open-chain adducts tended to form at higher reaction temperatures, or when polar reaction solvents were used.

The results obtained using tricyanoethylene and *N,N*-dimethylvinylamine and *N,N*-dimethylisobutenylamine can be explained in the framework of zwitterionic intermediates (Scheme III).

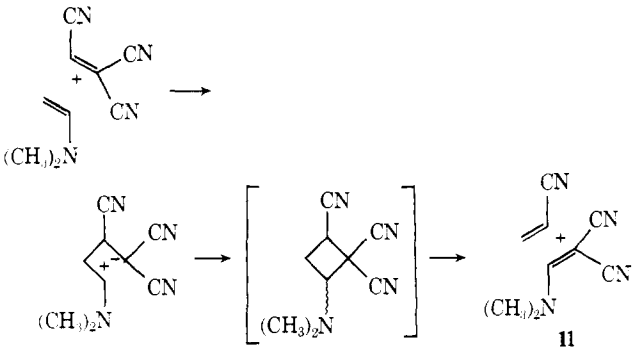
One molecule of tricyanoethylene (**1**) reacts with one molecule of enamine **5** to give the dipolar intermediate shown, which can cyclize to cyclobutane.

The dipolar intermediate can add a second molecule of tricyanoethylene to give 1-*N,N*-dimethylamino-2,2,3,

4,4,5-hexacyano-6,6-dimethylcyclohexane which is stable at −60°. At higher temperatures, it forms **12** by loss of hydrogen cyanide. The proclivity of the dimethylamino group to conjugate with a cyano group in **12** is apparent; steric crowding is probably also involved. The evolved HCN reacts with enamine **5** to give propane **13**.[21]

The novel feature of these results lies in the facile formation of olefin **11**.

Cleavage of cyclobutane to **11** and 1-cyanoisobutene (not isolated) is no doubt the pathway for its formation. The reaction pathway for *N,N*-dimethylvinylamine and TrCNE probably again involves the formation of an unstable cyclobutane which cleaves to the olefin **11**. Acrylonitrile, the presumed other product of this olefin metathesis reaction, was not isolated; it probably oligomerized in the basic medium.



11

No doubt, resonance stabilization of **11** is responsible for these extremely facile cleavages. Compound **11** has been obtained previously from another unusual reaction, that of *N,N*-dimethylformamide with malononitrile in the presence of acetic anhydride.[17] In order for this resonance to manifest itself in lowering the energy of the transition state, the cleavage should be concerted. A concerted $_{\pi}2_s + {}_{\pi}2_a$ cleavage would be thermally allowed; alternatively the strong electronic effects of the substituents may cause the Woodward–Hoffmann treatment to be inappropriate.[18-20]

In any case, as the respective electrophilic and nucleophilic properties of the olefins increase strongly, olefin metathesis becomes unexpectedly facile. However, as noted in the introductory section, the most electron-rich olefin reacts with the most electron-poor partner by redox reaction.[5] The boundary between these types of reaction remains to be elucidated.

Experimental Section

General. All boiling points and melting points are uncorrected. Capillary melting points were determined on a Thomas-Hoover melting point apparatus. Infrared spectra were determined with a Perkin-Elmer Model 337 spectrophotometer in KBr or between NaCl plates (the wavelengths are given in cm^{-1}). Nmr spectra were obtained on a Varian T60 spectrometer. Chemical shifts are reported on the τ scale. The mass spectra were measured on a Hitachi Perkin-Elmer RMU-6E double-focusing instrument. Samples nonvolatile below 100° were injected directly. The ionization potential was 70 eV. The gas chromatograms were obtained on a Varian Aerograph 1700 instrument using the following columns: (A) 3% SE 30 on 80-100 mesh Chromosorb W AW/DMCS HP, 5 ft × 0.25 in.; (B) 15% fluorosilicon QF-1-0065 on 80-100 mesh Anakron SD, 5 ft × 0.25 in.; (C) 5% Carbowax 20M on 80-100 mesh Chromosorb W AW/DMCS, 5 ft × 0.25 in.

Reactants. Tricyanoethylene (1) was synthesized according to the procedure of Dickinson, Wiley, and McKusick[22] and Noren.[23] As described in those papers, the amide must be synthesized at a temperature of −5° and be completely dry before dehydration; to completely consume the ethanetricarbonitrile, a 5% excess of bromine was used; dilution of the triethylamine in ether was advisable in small runs of dehydrohalogenation.

Dehydrobromination of 1-Bromoethane-1,1,2-tricarbonitrile. In a 250-ml three-necked flask fitted with a motor-driven stirrer and an addition funnel were placed 10 g of 1-bromoethane-1,1,2-tricarbonitrile (54.3 mmol) and 60 ml of ether. To the cold solution (<0°) was added dropwise 4.8 g of triethylamine (47 mmol) in 30 ml of ether. The addition time was approximately 30 min. The reaction mixture was filtered through a sintered glass filter funnel, the residue being thoroughly washed with ether. After rotary evaporation of the ether, the crude tricyanoethylene (**1**) was chromatographed on 35 g. of Woelm acidic alumina and eluted with ether. The first 120 ml contained the purified olefin which was isolated by rotary evaporation of the solvent as a yellow oil (sometimes as a white solid); yields of ~60% were usual.

Ethyl 2,3-Dicyanoacrylate (2). This compound was synthesized according to Noren's procedure.[23]

Dimethyl Cyanosuccinate.[24] To 178.2 g of methyl cyanoacetate (1.8 mol) dissolved in 750 ml of absolute methanol was added (under cooling) 41.4 g of sodium (1.8 mol). To the cold solution was added 68.1 g of methyl chloroacetate (0.6 mol) dissolved in 150 ml of absolute methanol (addition time 5 min, 10°). The mixture was stirred for 24 hr. The reaction mixture was put in a mixture of 1500 g of ice and 225 ml of concentrated hydrochloric acid. To this mixture was added 400 ml of water. This was divided in two fractions of ~1250 ml each. Each was extracted three times with 450 ml of dichloromethane, the organic layer was backwashed once with 200 ml of water, dried overnight over calcium sulfate, filtered, evaporated, and distilled under vacuum to give 54.8 g of crude product [bp 92° (0.5 mm), 90° (0.3 mm)]. Redistillation gave 47.95 g of pure product [47% yield, bp 78° (0.05 mm)].

Dimethyl 1-Bromo-1-cyanosuccinate.[24] In a 250-ml three necked flask fitted with a mechanical stirrer were placed 11.7 g of dimethyl cyanosuccinate (68.4 mmol), 100 ml of carbon tetrachloride, and 0.13 g of benzoyl peroxide. Under strong stirring, 4.1 ml of bromine (75 mmol) were added portionwise under visible light irradiation. Irradiation was maintained for 3 hr. Rotary evaporation gave 17.1 g of a red oil containing 80% of the brominated ethane (57.8 mmol).

Dimethyl 1-Cyanoethylene-1,2-dicarboxylate (3).[24] To the crude bromide (57.8 mol) dissolved in 100 ml of ether was added dropwise under cooling (bath temperature ~5°) 5.8 g of triethylamine (57.8 mmol). The reaction mixture was kept for 30 min at 5° and for 45 min at room temperature, then filtered and rotary evaporated. The crude product (generally oily, sometimes solid) was distilled under reduced pressure to give 6.47 g of product [92% pure, bp 124-138° (0.3 mm)] that crystallized. Recrystallization from ether gave the pure product in 40% yield starting from the ethane (4.65 g): mp 60-61°; ir (NaCl neat) 3150 (=C—H), 2226 (C≡N), 1730 (C=O), 1630 (C=C); nmr ($CDCl_3$) 2.57 (s, 1), 6.05 (s, 3, COOMe), and 6.09 (s, 3, COOMe).

Anal. Calcd for $C_7H_7NO_4$: C, 49.71; H, 4.17; N, 8.28; O, 37.84. Found: C, 49.55; H, 4.06; N, 8.20; O, 37.80.

Structure of Dimethyl 1-Cyanoethylene-1,2-dicarboxylate (3).[24] Nmr spectra of the crude reaction mixtures from several runs showed only one isomer, which on work-up was isolated in pure form. Comparing the experimental nmr absorption of the vinylic hydrogen with the calculated value[25] favored the fumarate structure for compound **3**. However, caution must be used in applying this method to trisubstituted olefins.

Trimethyl Ethane-1,2,2-tricarboxylate.[24] Dimethyl malonate, 188.4 g (1.545 mol) in 1500 ml of absolute methanol, was placed in a 3-l. four-necked flask fitted with a mechanical stirrer and a reflux condenser; 34.5 g of sodium (1.5 mol) was added in small pieces to the cooled solution. When all the sodium had reacted, 162.75 g of methyl chloroacetate (1.5 mol) was added dropwise (addition time ≃ 30 min); the temperature was kept below 2°. After 10 hr of reaction, the solvent was evaporated, and 350 ml of water was added. The organic layer was separated and the water layer extracted twice with 100 ml of ether. The combined organic layers were dried over magnesium sulfate, filtered, evaporated, and distilled on a spinning band to give 123.8 g of pure compound [41% yield, bp 83° (0.3 mm), 82° (0.18 mm)]: ir (NaCl neat) 1720 and 1690; nmr ($CDCl_3$) 6.33 (t, J = 7 Hz, 1), 7.20 (d, J = Hz, 2), 6.40 (s, 6, COOMe), and 6.47 (s, 3, COOMe).

Trimethyl 1-Bromoethane-1,1,2-tricarboxylate.[24] In a 2-l. three-necked flask fitted with a mechanical stirrer, an addition funnel and a reflux condenser were placed 98.6 g of trimethyl ethanetri-

carboxylate (0.48 mol), 800 ml of carbon tetrachloride, and 0.4 g of benzoyl peroxide. Stirring was begun, and 29.0 ml of bromine (0.53 mol) was added portionwise under visible light irradiation. After 24 hr, the solution was rotary evaporated. The crude bromide (148 g, 0.48 mol) was not purified and was used immediately; ir (NaCl, neat) 1740 and 1720 (COOMe), 650 (C-Br); nmr ($CDCl_3$) 6.23 (s, 6, COOMe), 6.38 (s, 3, COOMe), and 6.62 (s, 2).

Trimethyl Ethylenetricarboxylate (4).[24] To the crude bromide (148 g, 0.48 mol) dissolved in 600 ml of ether and cooled in an ice-water bath was added dropwise and with stirring 48.48 g of triethylamine (0.48 mol). The mixture was stirred for 2 hr and washed three times with 250 ml of water, and the water was backwashed (3×) with 100 ml of ether. The combined ether layers were dried over magnesium sulfate, filtered, evaporated, and distilled to give the olefin **4** [bp 87-90° (0.2 mm)]. The product crystallized on standing and was recrystallized from ether to give 58.5 g (60% yield): mp 39.5-40.5°; ir (NaCl neat) 1725 (COOMe), 1650 (C=C); nmr ($CDCl_3$) 3.12 (s, 1, =C—H), 6.12, 6.15, and 6.20 (3s, 9, COOMe).

***N,N*-Dimethylisobutenylamine (5).** Our procedure to synthesize *N,N*-dimethylisobutenylamine (**5**) is a variant of the one of Opitz.[12a] Dimethylamine (132 ml, 90 g, 2 mol) was condensed at Dry Ice temperature in a 1-l. three-necked flask fitted with a mechanical stirrer, a Dry Ice condenser, and a drying tube. Two hundred milliliters of ether and 72 g of isobutyraldehyde (1 mol) were cooled at Dry Ice temperature and added. Anhydrous potassium carbonate, 70 g, was added, and the reaction mixture was stirred for 60 hr, filtered, the precipitate being washed with ~75 ml of ether. The nmr spectrum taken at this point showed that the crude product was the aminal. Distillation in a glass helix packed column gave the desired product **5** in 46% yield [45.8 g, bp 86-87° (lit.[12c] 87°; lit.[12b] 87-88°)].

***N,N*-Dimethylpropenylamine (6).** *N,N*-Dimethylpropenylamine (**6**) was synthesized as **5**. Starting from 1 mol of aldehyde we obtained, after distillation at aspirator pressure, 22.3 g of enamine containing ~10% aminal. It was used without further purification.

***N,N*-Dimethylvinylamine (7)** was synthesized according to Dittmer's procedure.[13] Distillation at aspirator pressure (room temperature) gave a product containing always ether and some dimethylamine; redistillation with a cold distillation apparatus (helix packed column of 38-cm length) led to the removal of dimethylamine and a 79:21 mixture of *N,N*-dimethylvinylamine and ether [bp −28 to −22° (25 mm)] was obtained.

tert-Butyl vinyl ether (**8**) and methyl vinyl sulfide (**9**) are K&K products.

Trimethylsilyl Vinyl Ether (10). In a 2-l. three-necked flask fitted with a mechanical stirrer, a reflux condenser, and an addition funnel were placed 500 ml of xylene, 455 g of *N,N*-diethylcyclohexylamine (3 mol), 125 ml (45.9 g, 2.18 mol) of acetaldehyde, and 12 g of freshly fused zinc chloride. Trimethylchlorosilane (380 ml, 324 g, 3.0 mol) was added dropwise at a rate that maintained a gentle reflux (~1 hr). The mixture was then refluxed while being stirred for 48 hr. A mixture consisting of mainly trimethylchlorosilane and trimethylsilyl vinyl ether was distilled directly from the pot (bp up to 85°). Spinning-band distillation (2-ft column) gave 179 g of trimethylchlorosilane and 44.4 g of trimethylsilyl vinyl ether (**10**) (17%, bp 71-73°).

Reaction of *N,N*-Dimethylisobutenylamine with Tricyanoethylene. (a) At 0°. To a solution of 1.90 g of tricyanoethylene (18.4 mmol) in 10 ml of ether cooled at 0° was added 1.82 g of *N,N*-dimethylisobutenylamine (18.4 mmol). A very vigorous reaction occurred, and a black-brown product precipitated. The reaction mixture was extracted with 100 ml of ether. From this solution were isolated 0.05 g of 1,1-dicyano-2-*N,N*-dimethylaminoethylene (**11**) and 0.25 g of 1-*N,N*-dimethylamino-1-cyano-2-methylpropane (**13**) (containing a very small amount of **11**). Distillation of **13** gave a pure sample: bp 60° (25 mm) [lit.[21] 54° (1 mm)]; ir (NaCl neat) 2815, 2770 (Me_2N-), 2240 and 2220 (vw, C≡N); nmr ($CDCl_3$) 6.9-7.15 (two d, 1 H α to C≡N and Me_2N), 7.72 (s, 6 H, Me_2N), 7.87-8.40 (m, 1 H α to the 2 Me), 8.83-9.07 (two d, Me α to C-H); from the nmr spectrum, it seems there were two rotational isomers; mass spectrum (*m/e*, %) $M^{\cdot+}$ (126, 52), $M^{\cdot+}$ − HCN (99, 21), $M^{\cdot+}$ $-CH_2$=N-Me (83, 100).

The precipitate was recrystallized from 10 ml of ethyl acetate to give 0.16 g of cyclohexene **12** (6% yield).

(b) At −60°. To a solution of 1.55 g of tricyanoethylene (15 mmol) dissolved in 12 ml of toluene cooled at −60° was added 1.50 g of *N,N*-dimethylisobutenylamine (15 mmol) cooled at −60°. A red color developed instantly. The solution was kept for 2 days at −60°, then allowed to warm to room temperature. A brown-black precipitate formed that was filtered, washed twice with 60 ml of boiling ether, and recrystallized from 10 ml of ethyl acetate. Cyclohexene **12** (0.69 g, 32% yield) begins to decompose at 270° (end at 305°): ir (KBr) 2330, 2275 (vs conjugated C≡N), 1655 (vs conjugated C=C); nmr (DMSO-d_6) 6.02 (s, less than 1 H, 2 H α to cyano), 6.79 (s, 6 H, Me_2N-), 8.78 and 8.97 (two s, 6 H, Me_2C<); mass spectrum (*m/e*, %) $M^{\cdot+}$ (278, 90).

Anal. Calcd for $C_{15}H_{14}N_6$: C, 64.73; H, 5.07; N, 30.20. Found: C, 64.68; H, 5.09; N, 30.28.

Cycloaddition of *N,N*-Dimethylisobutenylamine and Ethyl 2,3-Dicyanoacrylate. To *N,N*-dimethylisobutenylamine (5.94 g, 60 mmol) cooled in a Dry Ice box (−55° to −60°) was added portionwise 3.00 g of ethyl 2,3-dicyanoacrylate (20 mmol) dissolved in 10 ml of ether and cooled at −30 to −40°. Keeping the flask and the addition funnel at lower temperature would precipitate the electron-poor olefin. At the beginning of the addition, a red-brown color developed which soon turned deep blue. After less than 1 hr, a blue oil precipitated. After several hours, the crystals of cycloadduct **14a** began to precipitate in the solution, then in the blue oil. After 1 day, their growth was finished; if there were no crystals, it was possible to initiate the crystallization by cooling the reaction mixture to −78°. The crystals were filtered as fast as possible and kept at Dry Ice temperature in a weighed vial. The crude **14a** could be kept for several days at Dry Ice temperature. If kept at room temperature, the cycloadduct decomposed in ~1 hr. It was impossible to isolate the product in purity. The absorptions are thus interpreted by comparison with the absorptions of the decomposed product and of the cycloadduct **14b** obtained from dimethyl 1-cyanoethylene-1,2-dicarboxylate and *N,N*-dimethylisobutenylamine: nmr ($CDCl_3$) 5.67 (2, q, J = 7.3 Hz, $COOCH_2$), 6.68 (1, s, H α to CN), 7.23 (1, s, H α to Me_2N), 7.80 (6, s, Me_2N).

Ethyl 4,4-Dimethyl-3-trimethylammonio-1,2-dicyanocyclobutane-2-carboxylate Trifluoromethanesulfonate (15a). The cold (−78°) crude cycloadduct **14a** (4.55 g, 18.3 mmol) was dissolved in 9 ml of cold (−78°) dichloromethane and added to 3.00 g of cold (−78°) methyl trifluoromethanesulfonate (18.3 mmol). After 40 min at −78°, the reaction mixture was kept overnight at −15°. The color turned from green to orange, and the salt **15a** precipitated. Addition of 2 ml of ether gave some more salt, yield 1.41 g, 19%. The salt was recrystallized from a mixture of acetonitrile, dichloromethane, and ether: mp 166-167.5°; ir (KBr) 2255 (-C≡N), 1750 (COOEt), 1244, 1160, 1138, 1026, and 632; nmr (DMSO-d_6) 5.45 (1, s), 5.68 (2, q, J = 7 Hz, $COOCH_2$), 5.93 (1, s), 6.67 (9, s, Me_3N^+), 8.26 (3, s, Me), 8.56 (3, s, Me), and 8.70 (3, t, J = 7 Hz, CH_3).

Anal. Calcd for $C_{15}H_{33}F_3N_3O_5S$: C, 43.58; H, 5.36. Found: C, 43.72; H, 5.34.

Cycloaddition of *N,N*-Dimethylisobutenylamine and Dimethyl 1-Cyanoethylene-1,2-dicarboxylate. To 1.98 g of *N,N*-dimethylisobutenylamine (20 mmol) cooled at −15° was added dropwise a solution of 1.69 g of dimethyl 1-cyanoethylene-1,2-dicarboxylate (10 mmol) in 20 ml of ether cooled at 5°. The reaction was finished in less than 15 min (nmr). Rotary evaporation (bath temperature <35°) left a moist white solid consisting of cycloadduct **14b** and some enamine. Addition of 10 ml of ether, filtration of the pure **14b**, and crystallization of the filtrate gave 2.11 g of pure cycloadduct **14b** (78% yield); the compound is not very stable thermally: mp 78-82°; ir (KBr) 2820 (Me_2N), 2240 (C≡N), 1720 (COOMe); nmr ($CDCl_3$) 6.17 and 6.25 (2s, 6, COOMe), 6.83 (s, 1, H α to COOMe), 7.33, 7.53, and 7.63 (3s, 2.3, containing H α to Me_2N and some Me_2N), 7.82 (s, 4.5, Me_2N), 8.27-8.97 (5s, 1.5, Me), and 8.67 (s, 4.5, Me).

Anal. Calcd for $C_{13}H_{20}N_2O_4$: C, 58.19; H, 7.51; N, 10.44. Found: C, 58.02; H, 7.44; N, 10.30.

Dimethyl 4,4-Dimethyl-3-trimethylammonio-2-cyanocyclobutane-1,2-dicarboxylate Trifluoromethanesulfonate (15b). To 13.7 g of *N,N*-dimethylisobutenylamine (138 mmol) at −15° was added dropwise 19.25 g of dimethyl 1-cyanoethylene-1,2-dicarboxylate (113.9 mmol) dissolved in 230 ml of ether over 40 min. At the end of the addition, some precipitating olefin **3** was present as a solid. The mixture was kept 5 min more at −15°, then carefully rotary

evaporated (bath temperature <28°). The excess enamine was removed under high vacuum (after 5 min, the pressure was 0.2 mm). Dichloromethane, 55 ml, was added, and the solution was cooled at −78° for 5 min and was then added to 18.7 g of cold (−78°) methyl trifluoromethanesulfonate (114 mmol). The reaction was kept for 10 min at −78° and overnight at −15° (freezer). The salt **15b**, 31.85 g, was obtained (65% yield); the salt was recrystallized from a mixture of dichloromethane, acetonitrile, and ether: mp 170–171°; ir (KBr) 1725 (COOMe), 1240, 1150, 1023, 630; nmr (DMSO-d_6) 5.55 (s, 1), 6.13 (s, 3, COOMe), 6.28 (s, 3, COOMe), 6.57 (s, 1.7), 6.69 (s, 8, Me_3N^+), 8.40 (s, 3, Me) and 8.51 (s, 3, Me).

Anal. Calcd for $C_{15}H_{23}F_3N_2O_7S$: C, 41.66; H, 5.37. Found: C, 41.82; H, 5.24.

A second product, mp 169°, was noted in the alkylation but has not been finally identified.

Cycloaddition of *N,N*-Dimethylisobutenylamine and Trimethyl Ethylenetricarboxylate. To 2.02 g of trimethyl ethylenetricarboxylate (10 mmol) dissolved in 10 ml of ether was added 0.99 g of *N,N*-dimethylisobutenylamine (10 mmol). A yellow-orange color developed which disappeared completely after 1 day. At this time the reaction was finished (nmr). After rotary evaporation of the solvent, the residue was kept at −20° and gave quantitatively the cycloadduct **14c**: melting range 44–51°; ir (KBr) 2825 and 2780 (Me_2N-), 1720 (COOMe); nmr ($CDCl_3$) 6.15–6.43 (9, COOMe), 7.68 and 7.77 (2s, 6, Me_2N), 8.30 (s, 3, Me), 8.85 and 8.92 (s, 3, Me).

Anal. Calcd for $C_{14}H_{23}NO_6$: C, 55.80; H, 7.69; N, 4.65. Found: C, 55.70; H, 7.73; N, 4.50.

Trimethyl 3-Trimethylammonio-4,4-dimethylcyclobutane-1,2,2-tricarboxylate Trifluoromethanesulfonate (15c). A solution of 21.19 g of crude trimethyl-3-*N,N*-dimethylamino-4,4-dimethylcyclobutane-1,2,2-tricarboxylate (**14c**) (70.4 mmol) in 35 ml of ether was cooled at −78°; 11.55 g of methyl trifluoromethanesulfonate (70.4 mmol) was cooled at −78° and added to the above solution. Instantly there was an abundant precipitate. The reaction mixture was allowed to come progressively to room temperature. The precipitate was filtered and recrystallized from 135 ml of dichloromethane and 25 ml of acetonitrile to give 27.5 g of pure salt (**15c**) (84% yield): mp 143.5–145°; ir (KBr) 1725 (COOMe), 1240, 1150, 1028, 635; nmr (DMSO-d_6) 5.47 (s, 1), 6.28 (s, 3, COOMe), 6.50 (s, 7, COOMe and one other proton), 6.95 (s, 9, N^+Me_3), 8.48 (s, 3, Me), and 8.80 (s, 3, Me).

Anal. Calcd for $C_{16}H_{26}F_3NSO_9$: C, 41.29; H, 5.63. Found: C, 41.28; H, 5.73.

Trimethyl 3-Trimethylammonio-4-methylcyclobutane-1,2,2-tricarboxylate Trifluoromethanesulfonate (15d). A solution of trimethyl ethylenetricarboxylate (2.02 g, 10 mmol) in 10 ml of ether was added portionwise to 0.92 g of *N,N*-dimethylpropenylamine (containing 10 mmol of enamine) cooled at −78°. Each time after addition the solution turned orange, then went back to yellow after a short time. When the addition was finished one waited 2 min more. Thereafter the solution was added to 1.64 g of methyl trifluoromethanesulfonate (10 mmol). Instantaneous precipitation occurred. The reaction mixture was kept at −15° overnight, then filtered to give the crude salt **15d**. Repeated crystallizations from a mixture of dichloromethane, acetonitrile, and ether gave 1.32 g of pure salt (29%): melting range 152–157°; ir (KBr) 1720 (COOMe), 1240, 1145, 1022, and 620; nmr (DMSO-d_6) 5.55–5.82 (m, 1.5), 6.20 (s, 6, COOMe), 6.35 (s, 3, COOMe), 6.60–7.03 (m containing the large singlet of Me_3N^+ at 6.87), 8.55–8.80 (m, 3, Me).

Anal. Calcd for $C_{15}H_{24}F_3NO_9S$: C, 39.91; H, 5.36. Found: C, 39.69; H, 5.36.

Reaction of *N,N*-Dimethylvinylamine with Tricyanoethylene. To a solution of 1.40 g of tricyanoethylene (13.6 mmol) in 10 ml of toluene cooled at −55° was added 2.7 g of an ethereal solution of *N,N*-dimethylvinylamine (containing ~15 mmol of the desired enamine). The solution became instantly dark. After 1 day, the solution was allowed to warm to room temperature, and the solvents were evaporated under high vacuum. Extraction of the residue with ether gave 0.4 g (24%) of the olefin **11**. Recrystallization from ether gave an analytical sample: mp 82.5–82.8° (lit.[17] mp 83°); ir (KBr) 2205 and 2190 (vs C≡N), 1650 and 1630 (s conjugated C=C); nmr ($CDCl_3$) 2.93 (s, 1, =C—H), 6.67 and 6.81 (2s, 6, Me_2N).

Reaction of *N,N*-Dimethylvinylamine with Trimethyl Ethylenetricarboxylate. *N,N*-Dimethylvinylamine (1.20 g containing approximately 10 mmol of *N,N*-dimethylvinylamine, 2 mmol of ether, and 3 mmol of dimethylamine) was cooled at −55°. Trimethyl ethylenetricarboxylate (2.63 g, 13 mmol) dissolved in 10 ml of ether was cooled at −55° until precipitation occurred. It was then put at room temperature until it became a solution (the temperature of the solution was below 0° at that time). To that solution was added the cold enamine, and the reaction mixture was cooled at −55°. The first crystals of cyclobutane **16** appeared after more than 15 min. After 1 hr, no more precipitation occurred, and the precipitate was filtered. It became a slightly yellow oil at room temperature, that solidified in the refrigerator (2.42 g, 88%). The analytical sample of **17** (recrystallized from ether) had mp 44–46.5°; ir (KBr) 1720 (COOMe), 1650 (C=C); nmr ($CDCl_3$) 3.93 (d, J = 13 Hz, 1, olefinic proton α to Me_2N-), 5.88–6.66 (m, 3), 6.32 (s, 9, COOMe), 7.42 (s, 6, Me_2N).

Anal. Calcd for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13; O, 35.13. Found: C, 52.65; H, 6.89; N, 5.02; O, 35.36.

Reaction of *tert*-Butyl Vinyl Ether with Tricyanoethylene. To a solution of 3.7 g of tricyanoethylene (36 mmol) in 12 ml of benzene were added some *tert*-butylhydroquinone and 3.61 g of *tert*-butyl vinyl ether (36.1 mmol) in 10 ml of benzene. The solution became instantly orange and warm. After 1 day, the reaction was finished (nmr). Rotary evaporation and crystallization gave 4.93 g (68%) of cycloadduct **18a**. Recrystallization gave a mixture of isomers (mp 94–101°): ir (KBr) 2970, 2230 (C≡N), 1180, 1145, 1130, 905, 885; nmr ($CDCl_3$) 5.23–5.60 (m, 1, CH-O), 6.43–6.77 (m, 1), 6.98–7.42 (m, 2), and 8.68 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.45; N, 20.68. Found: C, 65.01; H, 6.57; N, 20.80.

Reaction of Methyl Vinyl Sulfide with Tricyanoethylene. To a solution of tricyanoethylene (2.06 g, 20 mmol) in 6 ml of benzene under argon was added some di-*tert*-butylhydroquinone (in the next runs the reaction was done without inhibitor) and a solution of methyl vinyl sulfide (1.48 g, 20 mmol) in 4 ml of benzene. The mixture became instantly dark and warm. After 3 hr, the reaction was finished (nmr). Rotary evaporation left an oil that was crystallized from ether to give 2.57 g (73%) of a mixture of cyclobutanes **18b** A and B. Recrystallization from ether left an insoluble material that was recrystallized from ethyl acetate. From ether, each cyclobutane A and B was isolated pure; from ethyl acetate, B was isolated. A had mp 66–68°; ir (KBr) 2945 (s), 2253 (s, -C≡N); nmr ($CDCl_3$) 5.63–6.30 (m, 2), 6.73–7.63 (m, 2), and 7.68 (s, 3, MeS).

Anal. Calcd for $C_8H_7N_3S$: C, 54.24; H, 3.95; S, 18.08. Found: C, 54.10; H, 3.87; S, 18.12.

B had mp 119–122°; ir (KBr) 2970 (s), 2925 (s), 2255 (s, -C≡N); nmr (CD_3COCD_3) 5.32–5.77 (m, 2), 6.63–7.60 (m, 2), and 7.68 (s, 3, MeS).

Anal. Calcd for $C_8H_7N_3S$: C, 54.24; H, 3.95; S, 18.08. Found: C, 54.13; H, 3.85; S, 18.11.

Dimethyl 1-Cyanoethylene-1,2-dicarboxylate with Methyl Vinyl Sulfide. Addition of methyl vinyl sulfide (1.48 g, 20 mmol) to 1.82 g (10.8 mmol) of dimethyl cyanoethylene-1,2-dicarboxylate at 28° caused an exothermic reaction. Ice chilling was applied, and the addition was completed in 30 min. After an additional 30 min at 28°, nmr examination of the product showed that both cyclobutane and linear olefinic adduct had been formed.

Reactions of Methyl Vinyl Sulfide with Trimethyl Ethylenetricarboxylate. (a) Trimethyl 1-Methylthiobut-1-enetricarboxylate (20). To 4.04 g of trimethyl ethylenetricarboxylate (20 mmol) in 10 ml of benzene was added 1.48 g of methyl vinyl sulfide (20 mmol). After 15 days at room temperature, 0.2 g of di-*tert*-butylhydroquinone was added, and the solution was heated in an oil bath at 65°. One week later, there was no reactant left. Rotary evaporation of the solvent left an oil that was crystallized from a mixture of *n*-pentane-ether to give 3.54 g of trimethyl 1-methylthiobut-1-ene-*trans*-3,4,4-tricarboxylate (**20**) (64%). Recrystallization from ether afforded the analytical sample: mp 68.5–70°; ir (KBr) 1750 and 1722 (COOMe), 1600 (C=C); nmr ($CDCl_3$) 3.70 (d, J = 14.5 Hz, 1, =CHS), 4.80 (d, further split into a doublet of doublet, 1, H—C=), 5.97–6.43 (m, 2), 6.28 (s, 9, COOMe), 7.79 (s, 3, MeS).

Anal. Calcd for $C_{11}H_{16}O_6S$: C, 47.82; H, 5.84; S, 11.58. Found: C, 47.71; H, 5.73; S, 11.69.

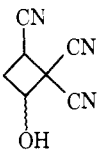
(b) Cyclobutane 19. Trimethyl ethylenetricarboxylate (2.02 g, 10 mmol) was dissolved in 1.48 g of methyl vinyl sulfide (20 mmol) at room temperature. After 3 days, the excess sulfide was evaporated with a vacuum pump and the residue crystallized from 5 ml of ether, yield 1.30 g (47%), mp from 54°. There was a small amount of liquid, most of the product melting at 69-74° (melting point of the ring opening product 68.5-70°); ir (KBr) 1730 (COOMe), 1650 and 1610 (?); nmr ($CDCl_3$) 4.47-4.77 (m, 1), 6.13, 6.30, 6.33 (3s, 9, COOMe), among these singlets one other proton (integration), 7.72 (s, 3, MeS), 7.52-8,05 (m, 2).

Anal. Calcd for $C_{11}H_{16}O_6S$: C, 47.82; H, 5.84; S, 11.58. Found: C, 47.68; H, 5.83; S, 11.73.

1,2,2-Tricyano-3-trimethylsiloxycyclobutane[16] (18c). To a solution of 2.3 g of tricyanoethylene (22 mmol) in 6 ml of benzene was added under argon a solution of 2.75 g of trimethylsilyl vinyl ether (23 mmol) in 4 ml of benzene. The reaction mixture became instantly yellow and warm. An nmr spectrum taken after 4 hr of reaction showed only the two isomeric cyclobutanes **18c** with an isomer ratio of 57:43. After rotary evaporation of the solvent and high vacuum evaporation of the last traces, the product was obtained in purity: ir (NaCl, neat) 2260 (C≡N), 1248, 840, 745 (all Me_3Si); nmr (C_6H_6) 5.15 and 5.66 (2t, J = 8 Hz, 1, CHOSi), 6.35-7.1 (m, 1), 7.4-7.85 (m, 2), 9.77 (s, 9, Me_3SiO).

Anal. Calcd for $C_{10}H_{13}N_3OSi$: C, 54.79; H, 5.93. Found: C, 54.90; H, 5.83.

When left in methanol for 30 min, this compound was completely methanolyzed to the tricyano alcohol **22.** No carbonyl function was detected by ir.



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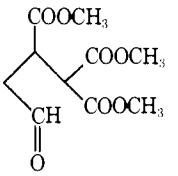
Trimethyl 3-Trimethylsiloxycyclobutane-1,2,2-tricarboxylate (21). Trimethyl ethylenetricarboxylate, 2.02 g (10 mmol), 2.32 g of trimethylsilyl vinyl ether (20 mmol), and 0.2 g of *tert*-butylhydroquinone were placed in an oil bath at 47° for 15 days (the reaction was followed by nmr). At that time, all the electron-poor olefin had reacted. Excess trimethylsilyl vinyl ether was evaporated. Attempts to separate the cycloadduct from the inhibitor (crystallization, chromatography, and distillation) failed.

When 8.08 g of trimethyl ethylenetricarboxylate (40 mmol), 9.30 g of trimethylsilyl vinyl ether (80 mmol), and 0.2 g of *tert*-butylhydroquinone were put in an oil bath at 63°, the reaction was finished after 1 week.

The colorless, slightly turbid oil **21** presented the following characteristics: ir (NaCl, neat) 2935, 1720 (COOMe), 1243, 840, and 750 (all Me_3Si); nmr (CCl_4) 4.53-4.80 (m, 1, CHOSi), 6.30-6.95 (3s, 9 COOMe and m, 1), 7.7-8.6 (m, 2), 9.8-10.1 (several s, 9, Me_3Si).

When left in methanol, the compound **21** hydrolyzed to aldehyde **23** (ring-opening product) in less than 30 min: nmr ($CDCl_3$) 0.27 (-C(H)=O).



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