5 is only significant (>0.01) at pH >5 under our conditions ($[Br^-] = 0.1$ M).

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Registry No. 1 ($R_1 = R_2 = H$), 66-22-8; 1 ($R_1 = R_2 = Me$), 874-44-6; 1 ($R_1 = H, R_2 = Me$), 608-34-4; 1 ($R_1 = Me, R_2 = H$), 615-77-0; 3 ($R_1 = R_2 = H$), 51-20-7; 3 ($R_1 = R_2 = Me$), 7033-39-8; 10 ($R_1 = R_2 = H$), 461-89-2; 10 ($R_1 = H, R_2 = Me$), 1627-30-1; 10 ($R_1 = R_2 = Me$), 15677-10-8.

Zwitterion Cycloadditions and Free-Radical Polymerizations of *p*-(Dimethylamino)styrene with Tris- and Tetrakis(carbomethoxy)ethylenes

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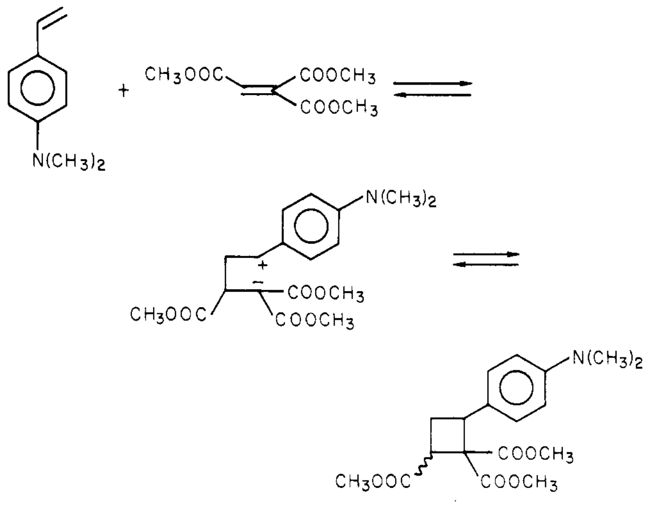
Tris- and tetrakis(carbomethoxy)ethylenes reacted with *p*-(dimethylamino)styrene to form cyclobutane cycloadducts. The reaction proceeded faster in polar solvents than in nonpolar solvents. This evidence supports a zwitterion intermediate in the cycloaddition reaction, but an intermediate could not be trapped with methanol, acetonitrile, or phenyl isocyanate. The cycloaddition reaction was not influenced by UV irradiation, radical inhibitors, or the one-electron oxidant ferric nitrate. These results are evidence against a possible cation-radical intermediate. Free-radical-initiated copolymerization occurred between tris- but not tetrakis(carboxymethoxy)ethylene and *p*-(dimethylamino)styrene to yield approximately alternating copolymers. These data are completely analogous to those obtained with other electron-rich styrenes and electrophilic trisubstituted ethylenes.

Both cycloaddition and polymerization reactions of electron-rich olefins with electron-poor olefins have been widely studied. Tetracyanoethylene has been known for a long time to react with olefins with a strongly electron-donating substituent, such as vinyl ethers, vinyl sulfides, vinylamines, and styrenes with electron-donating substituents in the para position.[1-4] Huisgen has extensively studied the reaction of tetracyanoethylene with vinyl ethers.[5-9] In this laboratory, the reaction of electron-deficient trisubstituted olefins such as tricyanoethylene with electron-rich olefins such as enamines and vinyl ethers has been studied.[10] These cyclobutane derivatives are mostly believed to arise from initial formation of a 1,4-zwitterion intermediate.

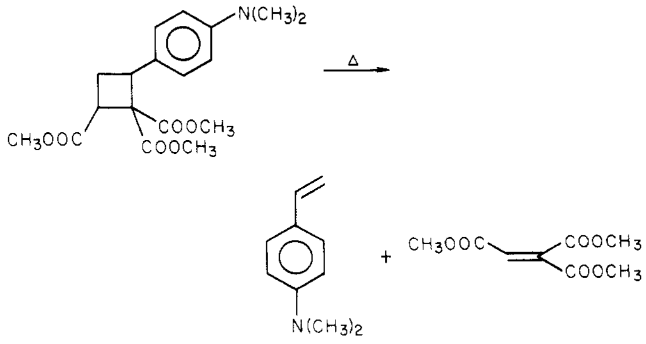
Regarding the polymerization reactions, neither tri- nor tetrasubstituted electrophilic ethylenes have been homopolymerized. Using free-radical initiations, the tri- but not the tetrasubstituted ethylenes smoothly copolymerize with electron-rich ethylenes to form 1:1 alternating copolymers.[11]

Recently, the highly electron-rich olefin *N*-vinylcarbazole was found to add to electrophilic ethylenes by a cation-radical route.[12] Accordingly, it was of interest to examine the still more electron-rich olefin *p*-(dimethylamino)styrene in cycloaddition and copolymerization reactions.

Scheme I



Scheme II



Results and Discussion

Intermediates. *p*-(Dimethylamino)styrene was prepared from the Grignard reaction of *p*-(dimethylamino)benzaldehyde and methyl iodide, followed by dehydration

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(1) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).

(2) P. D. Bartlett, *Q. Rev., Chem. Soc.*, 473 (1970).

(3) S. Nishida, I. Moritani, and T. Teraji, *J. Org. Chem.*, **38**, 1878 (1973).

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(5) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5054 (1973).

(6) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5056 (1973).

(7) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5058 (1973).

(8) R. Huisgen, *Acc. Chem. Res.*, **10**, 117 (1977).

(9) R. Huisgen, *Acc. Chem. Res.*, **10**, 199 (1977).

(10) H. K. Hall, Jr., and P. Ykman, *J. Am. Chem. Soc.*, **97**, 800 (1975).

(11) H. K. Hall, Jr., and R. C. Daly, *Macromolecules*, **8**, 22 (1975).

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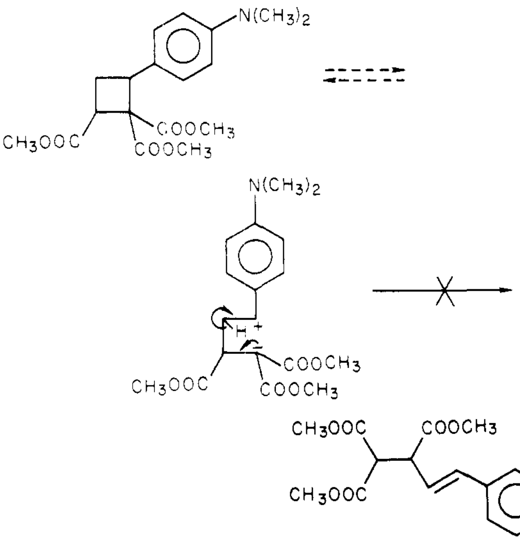
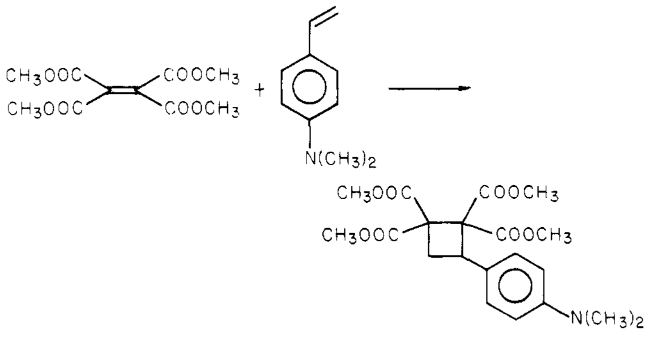
Scheme III



Scheme IV



of the resulting carbinol by flash distillation.[13] The electrophilic ethylenes were available from earlier investigations.[10,11]

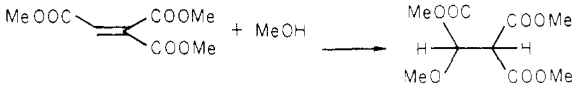
Reaction Products. The reaction of *p*-(dimethylamino)styrene with tris(carbomethoxy)ethylene[11] was investigated in different solvents. For example, 1 equiv of tris(carbomethoxy)ethylene reacted with 1 equiv of *p*-(dimethylamino)styrene at room temperature in acetonitrile to give 1-[*p*-(dimethylamino)phenyl]-2,2,3-tris(carbomethoxy)cyclobutane in 90% yield (Scheme I). The cyclobutane adduct was unstable. Attempts to purify the cyclobutane by vacuum distillation [150 °C (2 mmHg)] resulted in recovery of *p*-(dimethylamino)styrene and tris(carbomethoxy)ethylene (Scheme II).

Several attempts were made to isomerize the cyclobutane derivative to the thermodynamically more stable 1-butene.[10] The cyclobutane was heated to 150 °C for 4 h in dimethyl-d_6 sulfoxide (Me$_2$SO-d_6), but no 1-butene was formed (no vinyl protons were observed in the NMR spectrum) (Scheme III).

Tetrakis(carbomethoxy)ethylene was less reactive than tris(carbomethoxy)ethylene but gave cyclobutane in 59% yield after 16 h of reflux in acetonitrile (Scheme IV).

The reactivity of other (carbomethoxy)ethylenes was tested by mixing 1 equiv of methyl acrylate, dimethyl fumarate, and dimethyl maleate each with 1 equiv of *p*-(dimethylamino)styrene in refluxing acetonitrile. After several days the solvent was removed and the products were examined. The NMR spectra indicated that only starting materials were present.

Evidence for Zwitterion Mechanism. If cycloaddition proceeds via a zwitterion mechanism, the reaction should proceed fastest in the most polar solvent. Accordingly, the reaction of *p*-(dimethylamino)styrene with tris(carbomethoxy)ethylene was investigated in different solvents. The reactions were followed by NMR spectroscopy during 2 days. The rates were based on the appearance of two new peaks at δ 3.20 and 3.25 due to one of the carbomethoxy groups in the cyclobutane adduct. The signal of this methyl group is shifted to higher field due to the ring current of the phenyl group; two peaks appear because of the cis and trans isomers. The following sequence was obtained: 2-propanol, methanol > acetonitrile ≃ nitromethane > acetone > chloroform > benzene. [When methanol was used as a solvent, a side reaction occurred. When methanol and tris(carbomethoxy)ethylene were mixed and allowed to react for 12 h, the addition product was obtained:



This reaction, though, proceeded slower than the cycloaddition. With 2-propanol, this reaction did not occur.]

Although the solvent dependence of rate supported a zwitterionic intermediate, we were unable to trap the latter.

Huisgen[9] was able to trap the zwitterionic intermediate in the addition of tetracyanoethylene to propenyl ethers with ethanol to obtain the open-chain acetal. Trapping could also be done with acetonitrile or benzalaniline. When tris(carbomethoxy)ethylene was reacted with *p*-(dimethylamino)styrene in methanol or in the presence of phenyl isocyanate, only cyclobutane was obtained and trapping of the 1,4-zwitterion was not observed. Similarly, refluxing tetrakis(carbomethoxy)ethylene with *p*-(dimethylamino)styrene in methanol for 16 h gave only cyclobutane adduct.

Evidence against the Radical-Cation Mechanism. As mentioned, one purpose for doing the study was to determine whether or not initial formation of a radical cation played any role in the reaction. Hall and Glogowski[12] suggested that *N*-vinylcarbazole formed radical cations which reacted with electron-deficient olefins to give 1-butene in inert solvents and cyclobutane in donor solvents. In the present system, the product formed was independent of the solvent and consisted only of cyclobutane.

The cycloaddition reaction was run, with acetonitrile as solvent, in a Vycor tube in a photochemical reactor in 254-nm ultraviolet light. A blank was run at the same temperature as the photochemical reactor (45 °C) in the absence of light. The NMR spectrum of the run in UV light and the blank showed no detectable differences. The reaction of *p*-(dimethylamino)styrene with tris(carbomethoxy)ethylene was also run in the presence of the radical scavengers 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide and di-*tert*-butyl nitroxide. Neither of these compounds had any effect on the formation of cyclobutane. These experiments indicate that the cycloaddition does not proceed via a cation-radical mechanism.

Asanumo et al.[14] studied the photochemical dimerization of *p*-(dimethylamino)styrene alone and proposed that the dimer arose from a radical cation. In polar solvents, they obtained the trans isomer and in nonpolar solvents, the cis isomer. In our laboratory, the dimerization was carried out in acetonitrile in the presence of the electron acceptor

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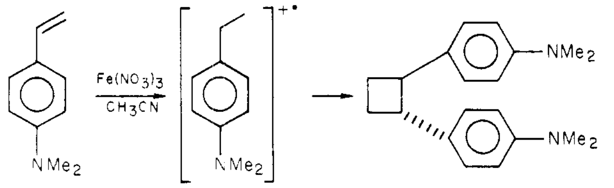
[13] R. H. Wiley and J. M. Schmitt, *J. Am. Chem. Soc.*, 80, 1389 (1958).

[14] T. Asanumo, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, 56 (1975).

Scheme V



$Fe(NO_3)_3$ and gave 1,2-trans cyclodimer in 81% yield in less than 0.5 h. When *p*-(dimethylamino)styrene was added to a solution of tris(carbomethoxy)ethylene and $Fe(NO_3)_3$ in methanol, the aminostyrene dimerized immediately leaving the tris(carbomethoxy)ethylene unaffected. These results again indicate that radical cations are not involved in the formation of the cyclobutane cycloadduct (Scheme V).

Free-Radical Copolymerization. Copolymers of *p*-(dimethylamino)styrene with methyl acrylate, dimethyl fumarate, dimethyl maleate, and tris(carbomethoxy)ethylene were prepared by reacting equivalent amounts of both monomers in benzene in the presence of azobisisobutyronitrile (AIBN) at 70 °C. Tetrakis(carbomethoxy)ethylene failed to give copolymer under these conditions. The results are summarized in Table I. From the results in Table I, it can be concluded that methyl acrylate, dimethyl fumarate, and tris(carbomethoxy)ethylene are almost equally reactive: the copolymer composition is almost the same with 40 to 45% incorporation of the ethylene in the polymer. Also, the yields are high for the methyl acrylate and dimethyl fumarate. The yield is lower for the tris(carbomethoxy)ethylene, because here the cyclobutane formation is a competitive reaction. Dimethyl maleate is less reactive: the yield is low and only 28% incorporation of the ethylene occurs. Tetrakis(carbomethoxy)ethylene is too sterically hindered to form polymer and also inhibits the homopolymerization of *p*-(dimethylamino)styrene.

Conclusions

In the reaction of tris(carbomethoxy)ethylene and *p*-(dimethylamino)styrene, cyclobutane arises from initial formation of a 1,4-zwitterionic intermediate, which undergoes rapid ring closure to give cyclobutane. This cyclobutane does not arise from a radical-cation intermediate. Of the (carbomethoxy)ethylenes studied in this experiment, only tris- and tetrakis(carbomethoxy)ethylenes gave cyclobutane adducts with *p*-(dimethylamino)styrene; apparently, these were the only two (carbomethoxy)ethylenes which were sufficiently electron-deficient to react with the electron-rich *p*-(dimethylamino)styrene. The cyclobutane adduct of *p*-(dimethylamino)styrene and tris(carbomethoxy)ethylene did not isomerize to the thermodynamically more stable 1-butene. The fact that the more polar solvents accelerated the cyclobutane formation sustains the theory that the reaction proceeds via a zwitterionic intermediate.

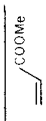
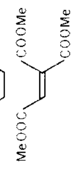
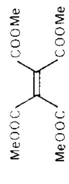
Methyl acrylate, dimethyl fumarate, dimethyl maleate, and tris(carbomethoxy)ethylene form copolymers with *p*-(dimethylamino)styrene in the presence of AIBN. Tetrakis(carbomethoxy)ethylene, on the other hand, did not copolymerize with *p*-(dimethylamino)styrene.

p-(Dimethylamino)styrene, therefore, behaves as a typical electron-rich styrene, and the behavior of *N*-vinylcarbazole in cycloaddition reactions[12] remains anomalous.

Experimental Section

Methods. NMR spectra were recorded on a Varian T60 nuclear magnetic resonance spectrometer. The infrared spectral data were

Table I. Copolymerization of *p*-(Dimethylamino)styrene with (Carbomethoxy)ethylenes

$Me_2NC_6H_4CH{=}CH_2$		comonomer				copolymer						
								elemental analysis				
wt, g	mol %	structure	wt, g	mol %	amt of AIBN, g	% yield[a]	η_{inh},[b] dL/g	% C	% H	% N	copolymer compn[c]	% cyclobutane yield
0.63	50		0.37	50	0.015	83	0.26	69.84	8.16	5.58	60/40	0
0.505	50		0.495	50	0.015	90	0.25	67.15	7.38	4.82	55/45	0
0.505	50		0.495	50	0.015	38	0.09	71.35	7.67	6.13	72/28	0
0.42	50		0.58	50	0.015	37	0.11	61.10	6.65	4.02	58/42	63
0.36	50		0.64	50	0.015	0						~5

[a] Yield after 16 h at 70 °C in 2 mL of benzene. [b] Inherent viscosity measured in chloroform at 30 ± 0.1 °C. [c] *p*-(Dimethylamino)styrene/comonomer.

obtained from a Perkin-Elmer 337 spectrophotometer. Chemical analyses were performed by Chemalytics, Inc., and by the University Analytical Center of the University of Arizona in Tucson.

***p*-(Dimethylamino)styrene.** Methyl iodide (60 g, 0.21 mol) in 500 mL of dry diethyl ether was added to 10 g (0.412 mol) of dry magnesium. After 1 h, 50 g (0.17 mol) of *p*-(dimethylamino)benzaldehyde in 400 mL of dry ether was added during 3 h. The obtained product was decomposed with a saturated ammonium chloride solution to which 5 mL of concentrated hydrochloric acid had been added. The carbinol was extracted and the solution dried over magnesium sulfate. The carbinol was dehydrated by flash distillation at 150 °C under vacuum. The water was removed by extraction and the product was dried and redistilled: bp 71–73 °C (0.1 mmHg) [lit.[13] 77–78 °C (2 mmHg)]; yield 15 g (60%).

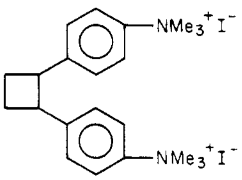
Electrophilic Olefins. These were prepared by literature procedures.[10,11]

1-[*p*-(Dimethylamino)phenyl]-2,2,3-tris(carbomethoxy)cyclobutane. *p*-(Dimethylamino)styrene (0.42 g, 2.85 mmol) was reacted with 0.58 g (2.85 mmol) of tris(carbomethoxy)ethylene in about 25 mL of acetonitrile. After overnight refluxing, the solvent was removed under reduced pressure to give the product as a yellow viscous oil in 30% yield (0.9 g): NMR ($CDCl_3$) δ 2.50 (m, 2 H), 2.80 (s, 6 H), 3.20 (s, 3 H), 3.25 (s, 3 H), 3.62 (s, 3 H), 3.63 (s, 3 H), 3.80 (s, 3 H), 4.30 (m, 1 H), 6.8 (dd, 5 Hz, 4 H); IR (KBr) 2960 (CH str), 1730 (C=O) cm^{-1}. The elemental analysis could not be performed on the cyclobutane due to its instability. The product was converted to the ammonium salt, which was prepared by adding excess methyl iodide to the cyclobutane oil. The mixture was stirred for 1 h and a white precipitate formed during this time. The excess methyl iodide was removed under reduced pressure and the salt was washed with a small amount of diethyl ether. The yield was 100%: NMR (D_2O) δ 3.2–3.8 (m), 3.55 (s), 4.5 (s), 7.6 (m); IR (KBr) 3450 (br), 3020 (CH), 2960 (CH), 1725 (C=O). Anal. Calcd: C, 46.45; H, 5.33; N, 2.85. Found: C, 46.66; H, 5.52; N, 3.12.

Attempts To Trap the Zwitterionic Intermediate. When 0.42 g (2.85 mmol) of *p*-(dimethylamino)styrene was reacted with 0.58 g (2.85 mmol) of tris(carbomethoxy)ethylene in 25 mL of methanol as solvent at room temperature or in 25 mL of phenyl isocyanate at 120 °C, only cyclobutane was obtained and no trapping of the 1,4-zwitterion was observed (determined by analysis of the end product by NMR spectroscopy).

Cycloaddition in the Presence of Radical Scavengers. *p*-(Dimethylamino)styrene (0.21 g, 1.42 mmol) and 0.29 g (1.42 mmol) of tris(carbomethoxy)ethylene were mixed in 1 mL of acetonitrile. In one run, 0.1 g of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide was added, and in a second reaction 0.1 g of di-*tert*-butyl nitroxide was used as a radical scavenger. The reaction mixtures were stirred overnight at room temperature. The NMR spectrum of the obtained cyclobutane was identical with the spectrum of a blank run in the same conditions.

Dimerization of *p*-(Dimethylamino)styrene. *p*-(Dimethylamino)styrene (0.5 g, 3.4 mmol) was dissolved in 25 mL of methanol, and 0.1 g of $Fe(NO_3)_3$ was added. A white precipitate formed almost immediately. The reaction was stirred at room temperature for 1.5 h. The precipitate was filtered. *trans*-1,2-Bis[*p*-(dimethylamino)phenyl]cyclobutane was obtained as a white solid (0.4 g) in 81% yield. The product was recrystallized from ether: NMR ($CDCl_3$) δ 2.2 (m, 4 H), 2.9 (s, 12 H), 3.6 (m, 2 H), 6.9 (dd, J = 45 Hz, 8 H). The elemental analysis again was performed on the ammonium salt prepared by adding excess methyl iodide to the dimer. Analysis for



Calcd: C, 45.69; H, 5.58; N, 4.84. Found: C, 45.35; H, 5.44; N, 5.00.

1-[*p*-(Dimethylamino)phenyl]-2,2,3,3-tetrakis(carbomethoxy)cyclobutane. A reaction mixture consisting of 0.64 g (2.46 mmol) of tetrakis(carbomethoxy)ethylene and 0.36 g (2.46 mmol) of *p*-(dimethylamino)styrene was refluxed for 16 h in 15 mL of acetonitrile. The solvent was removed under reduced pressure and a dark yellow oil was obtained.

The sample was dissolved in a minimum amount of ether and chloroform. After standing in the freezer overnight (16 h at −20 °C), the cyclobutane was obtained in 59% yield: mp 141 °C; NMR ($CDCl_3$) δ 2.5 (dd, J = 4.5 Hz, 2 H), 2.8 (s, 6 H), 3.2 (s, 3 H), 3.75 (s, 3 H), 3.82 (s, 6 H), 4.4 (dd, J = 4.5 Hz, 1 H), 6.90 (dd, J = 5 Hz, 4 H); IR (KBr) 2970 (CH str), 1750 (C=O) cm^{-1}. Anal. Calcd: C, 58.96; H, 6.19; N, 3.44. Found: C, 58.88; H, 6.35; N, 3.64.

Copolymerizations of *p*-(Dimethylamino)styrene with (Carbomethoxy)ethylenes. The two monomers were dissolved in 1 mL of benzene in the quantities indicated in Table I. The mixture was placed in a high-pressure tube which was capped and degassed. The reaction mixture was heated to 70 ± 1 °C during 16 h. The polymer was precipitated in excess methanol, filtered, dried, and weighed. The inherent viscosity was measured in chloroform at 30 ± 0.1 °C.

The yield of cyclobutane adduct is determined by NMR of the filtrate after evaporation of the solvents.

Acknowledgment. We are deeply indebted to the Polymers Program, Material Research, National Science Foundation (Grant No. DMR-78-09290) for support of this work.

Registry No. *p*-(Dimethylamino)styrene, 2039-80-7; methyl 2-propenoate, 96-33-3; dimethyl (*E*)-2-butenedioate, 624-49-7; dimethyl (*Z*)-2-butenedioate, 624-48-6; trimethyl ethenetricarboxylate, 51175-48-5; tetramethyl ethenetetracarboxylate, 1733-15-9; methyl iodide, 74-88-4; *p*-(dimethylamino)benzaldehyde, 100-10-7; 1-[*p*-(dimethylamino)phenyl]-2,2,3-tris(carbomethoxy)cyclobutane, 72541-97-0; 1-[*p*-(dimethylamino)phenyl]-2,2,3-tris(carbomethoxy)cyclobutane methiodide, 72541-98-1; *trans*-1,2-bis[*p*-(dimethylamino)phenyl]cyclobutane, 55980-59-1; *trans*-1,2-bis[*p*-(dimethylamino)phenyl]cyclobutane methiodide, 72541-99-2; 1-[*p*-(dimethylamino)phenyl]-2,2,3,3-tetrakis(carbomethoxy)cyclobutane, 72542-00-8.