oxide, 99.7%, was supplied by the Atomic Energy Commission. Potassium chloride and lithium chloride were Eastman red and white label. All salts were used as supplied.

Apparatus. Spectrophotometric kinetic measurements were conducted on a Beckman Model 5270 spectrophotometer equipped with an Acta M series autosampler. The sample cell was thermostated by circulated water at 30 ± 0.3 °C using a Precision Scientific Model 154 low temp temperature regulator. Measurements of the pH of the buffer solutions were conducted inside the temperature bath with a Sargent-Welch Model 830076 combination electrode. For reactions conducted in deuterium oxide, the pD was determined by adding 0.37 to the reading obtained for the glass electrode.[14]

Kinetic Procedure. Aqueous solutions buffered by succinimide/succinimide anion were prepared no more than 15 min before use by the addition of calculated amounts of standard aqueous potassium hydroxide to aqueous solutions of known concentrations of succinimide. The ionic strength of each buffer was maintained at 1 (unless otherwise stated) by addition of potassium chloride (except where lithium or tetramethylammonium chloride were used). Dilute dioxane solutions of the phenyl acetates were prepared and stored at 0 °C. A reaction was initiated in each buffer solution by addition of about 0.01 mL of the appropriate dioxane solution to 2.5 mL of the buffer in a cuvette. The cuvette containing the buffer had been previously thermostated in the cell holder of the spectrophotometer and, after momentary shaking, was returned to that position where absorbance due to the appropriate phenolate anion was measured by the instrument over an appropriate time period. The following wavelengths were employed: *p*-NO_2, 400 nm; *m*-NO_2, 350 nm; *p*-Cl, 285 nm; unsubstituted, 275 nm. The total succinimide concentration in the buffered solutions ranged from 0.1 to 1.0 M, while the concentration of phenyl acetate was always about 10^{-5} M. The pH of each buffer was recorded before and after each kinetic run. Each buffer was prepared to a pH tolerance of about 0.10 pH unit, while the pH drifted, on the average, 0.03 pH unit during the reaction. The values of K_w in water and in deuterium oxide at 30 °C that were employed were 1.48×10^{-14} and 2.24×10^{-15}, respectively. The pK_a values employed for succinimide in water and deuterium oxide were determined to be 9.51 and 9.95, respectively, at 1 M buffer by the method of half-neutralization. They agree with the value of 9.50 determined spectrophotometrically in water by Edwards and Terry.[4] Dilution of the buffer to 0.1 M solution resulted in a drift to lower pK_a' values of about 0.1 pH unit. Water used was doubly distilled from a glass apparatus.

A few experiments were conducted on the hydrolysis of succinimide itself similar to those of Edwards and Terry.[4] Aqueous 0.1 M potassium carbonate buffer solutions were prepared by dissolving calculated amounts of potassium carbonate and potassium bicarbonate in water. Three dilutions of this buffer were prepared containing 5×10^{-3} M succinimide. The rate of disappearance of succinimide was then measured spectrophotometrically at 235 nm at 30 ± 0.3 °C.

Pseudo-first-order rate constants were calculated using eq 12

$$k = \frac{\ln (OD_\infty - OD_0)/(OD_\infty - OD_t)}{t} \qquad (12)$$

with the aid of a weighted least-squares program written for an Oliveti-Underwood programmable 100 desk computer. Representative numbers of these computations were plotted to ensure that the reactions were indeed conducted under first-order conditions.

Acknowledgment. The financial support of the Northern Arizona University Institutional Research Committee and helpful discussions with Professors E. B. Hoyt, Jr., and G. Caple are gratefully acknowledged.

Registry No. PNPA, 830-03-5; MNPA, 1523-06-4; PCPA, 876-27-7; PA, 122-79-2; succinimide, 123-56-8; succinimide anion, 28627-67-0.

Reactions of *N,N*-Dimethylvinylamine with Electron-Poor Olefins

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Received April 12, 1982

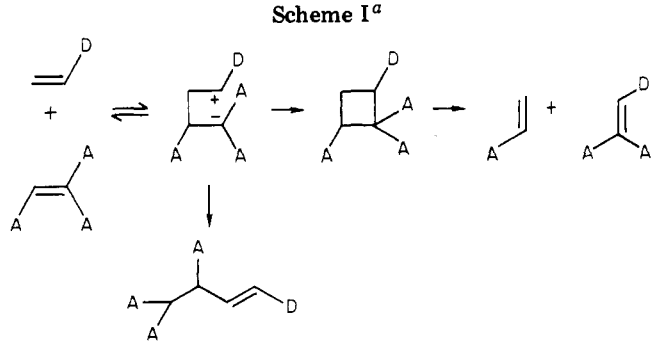
The reactions of *N,N*-dimethylvinylamine with electron-poor olefins have been studied. With 1,2-dicyanoethylene and *N*-phenylmaleimide, the cyclobutane adduct was obtained. Trimethyl ethylenetricarboxylate and tetramethyl ethylenetetracarboxylate yielded mostly an open-chain 1-butene derivative. At −90 °C reaction with trimethyl ethylenetetracarboxylate and subsequent treatment with alkylating agent yield the disalt of the 2:1 cyclohexane adduct and the salt of the metathesis product, the latter indicating the presence of cyclobutane at this temperature. We suggest that a zwitterionic intermediate can collapse to the cyclobutane, or rotate around the C_2–C_3 bond to form the 1-butene.

Introduction

Reactions of nucleophilic olefins such as enamines with olefins possessing varying electrophilic character give rise to various small molecule and polymer products. Hall and Ykman,[1] in their early study, reacted several vinylamines with trisubstituted electron-poor olefins. In certain conditions these isomerized to the thermodynamically favored 1-butene derivatives. Even uncatalyzed olefin metathesis was observed in a few cases. In these highly polar systems, the results were explained in the context of zwitterionic tetramethylene intermediates (Scheme I).

Cyclobutane formation from enamines has also been reported in the literature by Lewis and co-workers[2] in the reaction of *N*-isobutenylpyrrolidine with dimethyl fumarate, and by Fleming and Harley-Mason[3] in the reaction of *N,N*-dimethylisobutenylamine with acrylonitrile.

Scheme I[a]



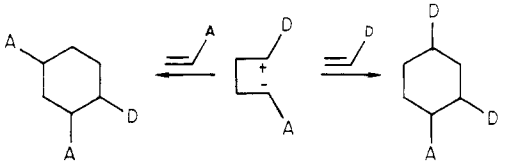
[a] D = NR_2, OR, SR; A = CN, $COOCH_3$.

(1) Hall, H. K., Jr.; Ykman, P. *J. Am. Chem. Soc.* **1975**, *97*, 800.
(2) Lewis, F. D.; Ho, T. I.; DeVoe, R. J. *J. Org. Chem.* **1980**, *45*, 5283.

0022-3263/82/1947-3691$01.25/0

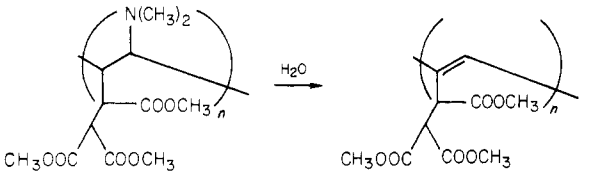
Kuehne and Foley[4] reacted the morpholine enamine derivative of cyclohexanone with nitroethylene and β-acetoxynitroethylene and in each case obtained a mixture of aminocyclobutanes and 1-butene derivatives. These [2 + 2] thermal cycloadditions were postulated to proceed via zwitterionic tetramethylene intermediates.

Structurally stablized zwitterions can add another molecule of either the electron-rich or the electron-poor olefin with eventual formation of cyclohexane derivatives. Among enamines, Brannock and his colleagues[5] observed the latter in the reaction of *N,N*-dimethylisobutenylamine with dimethyl 1,1-ethylenedicarboxylate. Cook[6] has reviewed the cycloaddition reaction of enamines in his book. In this study, we continue the study of the reactions of the very reactive *N,N*-dimethylvinylamine.



Results

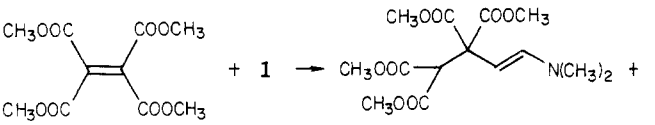
N,N-Dimethylvinylamine (1) was reacted in a 2:1 ratio with trimethyl ethylenetricarboxylate (2) at −55 °C in different solvents. Only the 1-butene derivative, trimethyl 1-(dimethylamino)-1-butene-3,4,4-tricarboxylate (3) was obtained in varying yields (40% yield in tetrahydrofuran, 52% in toluene, and 88% in diethyl ether;[1] Scheme II). At 0 °C in 1,2-dichloroethane only a 25% yield of 3 was obtained. The remaining product consists of oligomeric products, which gradually deaminate at room temperature. The 1-butene 3 is a solid at room temperature; it gradually decomposes to the same oligomeric products mentioned above. The spectra of these oligomers are in agreement with a polymeric vinylamine, which then deaminates in the presence of moisture.



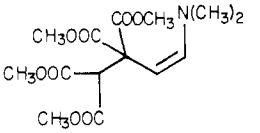
The reaction was repeated in equimolar amounts in ether at −20 °C. Because of the instability of the free amine 3 at room temperature, an alkylating agent, namely, methyl trifluoromethanesulfonate, was added to the reaction mixture. This resulted in (*trans*-1-butenyl)ammonium salt 4.

In an attempt to intercept a possible cyclobutane, the reaction was carried out in equimolar amounts at −90 °C, and an alkylating agent, dimethoxycarbenium hexafluorophosphate was added at this temperature. The diammonium salt of the 2:1 cyclohexane adduct 6 and the olefin metathesis product, dimethyl 1-(trimethylammonio)ethene-2,2-dicarboxylate hexafluorophosphate (5), were obtained. No cyclobutane derivatives were isolated.

Tetramethyl Ethylenetetracarboxylate (7). At 0 °C 1 and 7 react to form *trans*-8a and *cis*-1-butene 8b in tetrahydrofuran and toluene in very low yield; in 1,2-dichloroethane only the trans isomer 8a is formed in 4% yield. The trans isomer has been isolated but is unstable at room temperature. The remainder of the products form oligomeric products which again gradually deaminate. Attempts to run the reaction at lower temperature failed due to the insolubility of the tetraester 7.

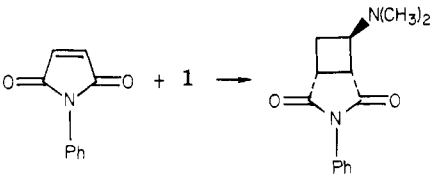


7 8a



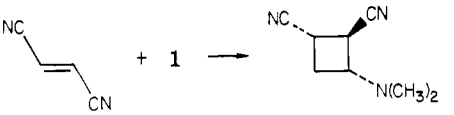
8b

***N*-Phenylmaleimide (9)** reacts with 1 in an equimolar ratio at −15 °C in acetonitrile to yield *N*-phenyl-3-(dimethylamino)-1,2-cyclobutanedicarboxamide (10) and oligomeric products. Only one isomer of 10 is obtained; the NMR data are not conclusive, but the trans structure has been assigned for steric reasons.



9 10

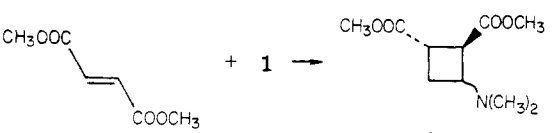
Fumaronitrile (11) reacts with 1 at −15 °C in acetonitrile to give 3-(dimethylamino)-1,2-dicyanocyclobutane (12).



11 12

Cyclobutane 12 is very unstable and could not be isolated. From the NMR spectrum it can be concluded that only one isomer is obtained. Although the data are not conclusive, the all-trans structure has been assigned for steric reasons.

Dimethyl fumarate (13) reacts with 1 in a 1:1 and 1:2 ratio at 0 °C in acetonitrile to yield exclusively dimethyl 3-(dimethylamino)-1,2-cyclobutanedicarboxylate (14). Attempts to isolate 14 resulted in decomposition of the product which is stable in solution.



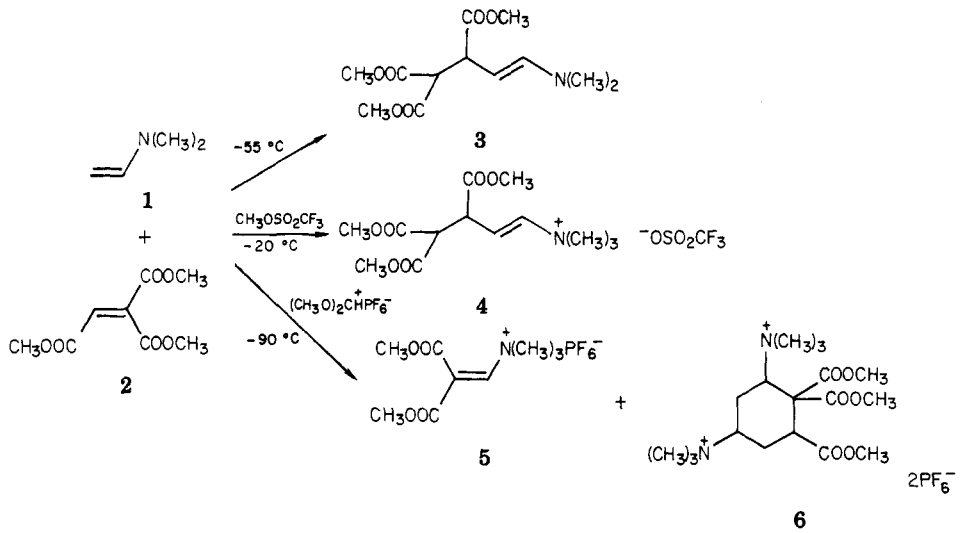
13 14

Discussion

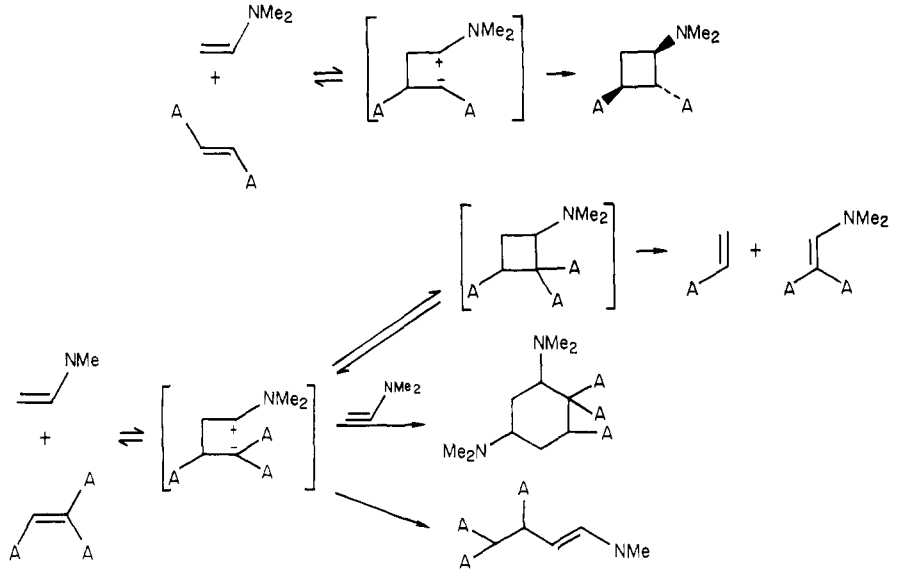
Reactions between electron-rich and electron-poor olefins proceed via a tetramethylene intermediate which is a resonance hybrid of a 1,4-zwitterion and a singlet biradical.[7] In the reactions with *N,N*-dimethylvinylamine,

(3) Fleming, I.; Harley-Mason, J. *J. Chem. Soc.* **1964**, 2165.
(4) Kuehne, M. E.; Foley, L. *J. Org. Chem.* **1965**, *30*, 4280.
(5) Brannock, K. C.; Bell, A.; Burpitt, R. D.; Kelley, C. A. *J. Org. Chem.* **1964**, *29*, 801.
(6) Cook, A. G. "Enamines"; Marcel Dekker, New York, 1969.

Scheme II



Scheme III

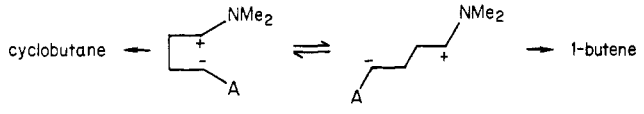


the tetramethylene is predominantly 1,4-zwitterionic regardless of the electrophilic partner (Scheme III).

Cyclobutanes are obtained with all the 1,2-disubstituted ethylenes. The cyclobutane adducts with *N*-phenylmaleimide and fumaronitrile are obtained in only one isomeric form. From the NMR spectra and steric considerations, we assume that only the 1,2-trans isomer is formed. With dimethyl fumarate, the NMR spectra are not very clear and more isomers could be present.

Trimethyl ethylenetricarboxylate is very reactive and only at −90 °C can we assume that the cyclobutane adduct has been formed. This adduct however cannot be isolated, not even when alkylating agent is being added to the reaction mixture. Only the metathesis product, formed from decomposition of the cyclobutane, and the 2:1 cyclohexane adduct, formed by reaction of the zwitterionic intermediates with a second *N,N*-dimethylvinylamine molecule, are obtained. Very effective stabilization of the charges in the zwitterionic intermediate by the amino group (and the two ester groups) accounts for these results.

At higher temperatures, the 1,4-zwitterionic intermediate can rotate around the C_2–C_3 bond to yield the extended form, in contrast with the coiled form which leads to cyclobutane.



Excessive steric interaction between the dimethylamino group and the two ester groups in the case of tri- and tetrasubstituted electron-poor olefins would favor the trans form of the zwitterion. Subsequent hydrogen shift leads to the 1-butene derivatives. This is consistent with the earlier results of Hall and Ykman.[1] No cyclobutane adducts could be isolated despite our more determined efforts with a variety of reaction conditions.

Experimental Section

Instrumentation. NMR spectra were recorded on a Varian EM 360L nuclear magnetic resonance spectrometer. Infrared spectra were recorded on a Model 710A Perkin-Elmer spectrophotometer. Elemental analyses were performed by the University of Arizona, Analytical Center in Tucson.

Reactants. Trimethyl ethylenetricarboxylate (**2**) and tetramethyl ethylenetetracarboxylate (**7**) were synthesized according to Daly's procedure.[8] The synthesis of *N,N*-dimethylvinylamine

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

(1) of Chang and Dittmer[9] was improved.

2-(Dimethylamino)ethyl Chloride. 2-(Dimethylamino)ethyl chloride hydrochloride (70 g, 0.486 mol) was dissolved in 50 mL of distilled water. In a second flask 40.9 g (0.725 mol) of potassium hydroxide was dissolved in 25 mL of distilled water. The two solutions were cooled in an ice bath and then mixed. An oil formed rapidly and was extracted with three 100-mL portions of ethyl ether. The ether solution was dried over magnesium sulfate. After filtration, the solvent was evaporated to yield 38.69 g (70%) of the crude free amine.

***N,N*-Dimethylvinylamine.** In a 2-L two-neck round-bottom flask equipped with a magnetic stirrer and distilling apparatus (lubricated with Lubriseal, not with silicone grease) were placed 44.44 g (0.396 mol) of potassium *tert*-butoxide and 500 mL of dimethylformamide. The reaction vessel was cooled in a methanol–ice bath. Crude 2-(dimethylamino)ethyl chloride (38.69 g, 0.36 mol) was added with stirring to the cold solution under argon atmosphere and the reaction was left for 20 min. Distillation at 2-mmHg pressure yielded 100 mL of a solution of *tert*-butyl alcohol and *N,N*-dimethylvinylamine in dimethylformamide in a receiver cooled by a dry ice–acetone bath. The 100 mL of solution was placed in a methanol–ice bath and fractionally distilled by use of a Vigreux column, a condenser, and a receiver chilled by dry ice–acetone. *N,N*-Dimethylvinylamine (1; 10.08 g, 39.4%) was obtained pure at 25 °C (35 mmHg) (it was stored at −50 °C and used within 24 h): NMR (DMF-d_6) δ= 2.7 (s, 6 H), 3.15–3.6 (m, 2 H), 5.9 (dd, J_{cis} = 8 Hz, J_{trans} = 14 Hz, 1 H).

General Procedure. All the reactions were run following the same technique. First 1 was injected in a capped test tube which was degassed previously and contained 1 mL of solvent. The sample was weighed, and the desired amount of electron-poor olefin was dissolved in 7 mL of the same solvent, degassed, and kept under argon atmosphere. Then the two test tubes were chilled to the desired temperature, and the 7 mL of solution was added to the solution of 1 with a syringe. The reaction was worked up after 48 h.

Trimethyl 1-(Dimethylamino)-*trans*-1-butene-3,4,4-tricarboxylate (3). Trimethyl ethylenetricarboxylate (2; 0.951 g, 4.7 mmol) was reacted with 1 (0.67 g, 9.4 mmol) in 8 mL of THF at −55 °C. After 48 h the solvent was evaporated. Trimethyl 1-(dimethylamino)-1-butene-3,4,4-tricarboxylate (3; 0.51 g, 40% yield) was recrystallized from a 1:1 mixture of pentane and diethyl ether and was unstable at room temperature: IR (KBr) 2925, 2850, 1720 (ester), 1640 (enamine) cm^{-1}; NMR ($CDCl_3$) δ 2.55 (s, 6 H), 3.7 (m, 11 H), 4 (dd, 1 H), 6.1 (d, J_{trans} = 14 Hz, 1 H). Anal. Calcd for $C_{12}H_{19}O_6N$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.23; H, 7.08; N, 4.92.

Trimethyl 1-(Trimethylammonio)-*trans*-1-butene-3,4,4-tricarboxylate Trifluoromethanesulfonate (4). Trimethyl ethylenetricarboxylate (2; 2.84 g, 14 mmol) and *N,N*-dimethylvinylamine (1; 1.0 g, 14 mmol) were mixed in 20 mL of diethyl ether at −78 °C and kept at that temperature for 2 h. After 18 h at −20 °C, the mixture was again cooled down to −78 °C for the addition of methyl trifluoromethanesulfonate (3.5 g, 15 mmol). A tarry precipitate formed at −20 °C and the solution was decanted. At room temperature, more precipitate formed and the solvent was evaporated. Dissolution in hot ethyl acetate and precipitation with pentane yielded a white precipitate: yield 1.3 g, 20%; mp 91.3–93.5 °C; NMR (Me_2SO-d_6) δ 3.4 (s, 9 H), 3.75 (s, 9 H), 3.4–4.2 (m, 3 H), 6.6 (dd, 1 H). Anal. Calcd for $C_{14}H_{21}NF_3SO_9$: C, 38.6; H, 4.8: N, 3.2. Found: C, 38.41; H, 4.91; N, 3.20.

Dimethyl 1-(Trimethylammonio)ethene-2,2-dicarboxylate Hexafluorophosphate (5). A solution of 1.42 g of *N,N*-dimethylvinylamine (1; 20 mmol) in 10 mL of pentane was slowly added at −90 °C to a solution of 4.04 g (20 mmol) of 2, also at −90 °C. The addition was carried out over a period of 2 h and was done under a nitrogen atmosphere. This was allowed to react at −90 °C for 2 h. Dimethoxycarbenium hexafluorophosphate (8.8 g, 40 mmol) was chilled to −90 °C and added as a solid to the reaction mixture and allowed to react for an additional 2 h at −90 °C. This was then warmed to room temperature (28 °C) and allowed to react overnight. The solids were filtered, washed with methanol, and filtered again. Recrystallized from an ethyl acetate–acetonitrile mixture gave 4.28 g (60%) yield of dimethyl 1-(trimethylammonio)ethene-2,2-dicarboxylate hexafluorophosphate (5): mp 173–175 °C. Anal. Calcd for $C_{10}H_{18}F_6NO_6P$: C, 31.12; H, 4.6; N, 4.0; P, 9.53. Found: C, 31.66; H, 4.84; N, 4.15; P, 9.55.

Trimethyl 3,5-Bis(trimethylammonio)cyclohexane-1,2,2-tricarboxylate Bis(hexafluorophosphate) (6). The filtrates from the previous reaction were combined with the methanol wash. This was then placed on a column consisting of activated carbon, cellulose powder, and Celite and eluted with ethyl acetate. The first material to come off the column was recrystallized from ethyl acetate to yield 0.64 g of 6 as a white solid: mp 224–245 °C. Anal. Calcd for $C_{18}H_{34}N_2F_{12}P_2O_6$: C, 32.53; H, 5.12; N, 4.22. Found: C, 32.63; H, 5.07; N, 4.38.

Tetramethyl 1-(Dimethylamino)-*trans*-1-butene-3,3,4,4-tetracarboxylate (8). Tetramethyl ethylenetetracarboxylate (7; 0.922 g, 4.15 mmol) was reacted with 1 (0.59 g, 8.3 mmol) in 8 mL of 1,2-dichloroethane at 0 °C under argon atmosphere in a capped tube. After 48 h of reaction the solvent was evaporated. The *trans*-1-butene 8a was recrystallized from a diethyl ether–pentane mixture (1:1) at −50 °C as crystals in a very small yield (4.1%, 0.03 g) because of the instability of the compound. 8: IR (KBr) 2950, 1720 (ester), 1640 (enamine) cm^{-1}; NMR ($CDCl_3$) δ 2.68 (s, 6 H), 3.8 (s, 12 H), 4.22–4.5 (m, 2 H), 6.28 (d, J_{trans} = 14 Hz, 1 H). The coupling constant for the *cis*-1-butene derivative 8b was 12 Hz. Anal. Calcd for $C_{14}H_{21}NO_8$: C, 50.75; H, 6.39; N, 4.23. Found: C, 51.09; H, 6.31; N, 3.98.

Reaction of 1 with *N*-Phenylmaleimide (9). *N*-Phenylmaleimide (9; 0.65 g, 3.75 mmol) was reacted with 1 (0.27 g, 3.75 mmol) at −15 °C in 8 mL of acetonitrile. After 48 h, the solvent was evaporated and diethyl ether was added. An oligomer of *N*-phenylmaleimide was obtained as a precipitate: yield 0.41 g, 63%; NMR (Me_2SO-d_6) only aromatic absorptions at δ 7.2 were visible; IR (KBr) 3050, 2850, 1650 (maleimide carbonyl) cm^{-1}. Anal. Calcd for $C_{10}H_7NO_2$: C, 69.3; H, 4.04; N, 8.09. Found: C, 68.01; H, 4.38; N, 8.35. After evaporation of the ether, pentane was added to the reaction product and more oligomeric products precipitated.

N-Phenyl-2-(dimethylamino)cyclobutane-1,2-dicarboximide (10) was obtained as an oil soluble in petroleum ether: yield 0.312 g, 31%; IR (KBr) 2925, 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.4 (s, 6 H), 2.7–3.1 (m, 4 H), 3.9 (dd, J = 6.4 Hz, J_2 = 8 Hz, 1 H), 7.2–7.6 (m, 5 H). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.56; H, 6.65; N, 11.60.

1-(Dimethylamino)-2,3-dicyanocyclobutane (12). Equimolar amounts of 1 and fumaronitrile (11) were mixed at 15 °C in acetonitrile. After 48 h diethyl ether was added and the solution was decanted from the formed oily precipitate. Cyclobutane 12 was not stable at room temperature. 12: NMR ($CDCl_3$) δ 2.3 (s, 6 H), 2.5–2.9 (m, 4 H), 3.8 (dd, J = 8 Hz, J_2 = 9 Hz, 1 H); IR (KBr) 2900, 2825, 2250 cm^{-1}.

Dimethyl 1-(Dimethylamino)cyclobutane-2,3-dicarboxylate (14). Equimolar amounts of 1 and dimethyl fumarate 13 were mixed at 0 °C in acetonitrile. Oligomeric products are removed by adding diethyl ether to the solution. Cyclobutane 14 is not stable at room temperature. 14: NMR ($CDCl_3$) δ 2.3 (s, 6 H), 2.5–2.8 (m, 4 H), 3.5–3.8 (m, 1 H), 3.6 (s, 3 H), 3.7 (s, 3 H); IR (KBr) 2925, 1720 cm^{-1}.

Acknowledgment. We are indebted to the Eastman Kodak Co. for the granting to M.E.G. of a Doctoral Study Award, to the Sonatrach Corp. (Algeria), and to the Materials Research Divison, National Science Foundation (Grant DMR 78-09290) for support of M.A.

Registry No. 1, 5763-87-1; 2, 51175-48-5; 3, 54821-86-2; 4, 82045-20-3; 5, 82045-22-5; 6, 82045-24-7; 7, 1733-15-9; 8a, 82056-48-2; 8b, 82045-25-8; 9, 941-69-5; 9 oligomer, 25101-57-9; 10, 82045-26-9; 11, 764-42-1; 12, 82045-27-0; 13, 624-49-7; 14, 82045-28-1; 2-(dimethylamino)ethyl chloride, 107-99-3.

(8) Hall, H. K., Jr.; Daly, R. C. *Macromolecules* **1975**, *8*, 22, 959.
(9) Chang, P. L.; Dittmer, D. C. *J. Org. Chem.* **1969**, *34*, 2791.