Photochemical Apparatus. Preparative irradiations employed a quartz immersion well and a Hanovia 450-W medium-pressure mercury-vapor lamp. Water jacketed vessels of 250 or 500 mL were used, and the solutions were purged continuously with a stream of oxygen-free nitrogen.[11] Analytical irradiations employed the same light source and immersion well, combined with a "merry-go-round" type apparatus with quartz photolysis tubes of ca. 15-mL capacity. Solutions (10 mL, 0.02 M in compound to be studied) were degassed with oxygen-free nitrogen[11] prior to irradiation.

3,3-Dideuterio-4-isochromanone. To a solution of 8.0 g (0.054 mol) of 4-isochromanone[12] in 40 mL of dry THF was added 40 mL of NaOD, prepared by reacting 0.4 g of sodium with 40 mL of D_2O. After the solution was stirred at room temperature for 20 min, the THF was removed in vacuo and the residue was extracted with dichloromethane. After the solution was dried over anhydrous Na_2SO_4, the solvent was removed in vacuo and the residue was treated as above a second time. Distillation gave 6.0 g (74%) of 3,3-dideuterio-4-isochromanone: NMR ($CDCl_3$) δ 4.87 (s, 2 H, benzylic H), 7.0–8.2 (m, 4 H, aromatic H). The singlet at δ 4.23 for the protons on C-3 of 4-isochromanone was entirely absent.

3-Deuterio-4-methylisochromene (1b). Compound **1b** was prepared from 3,3-dideuterio-4-isochromanone in the same manner[4] as the preparation of **1a** from 4-isochromanone: NMR ($CDCl_3$) δ 1.80 (s, 3 H, CH_3), 4.89 (s, 2 H, CH_2), 6.6–7.3 (m, 4 H, aromatics).

Methyl 2-(2-Methylphenyl)propanoate (4a). A solution of 0.15 g (0.91 mmol) of 2-(2-methylphenyl)propanoic acid[13] and 0.1 mL of H_2SO_4 in 5 mL of methanol was heated to reflux for 4 h. The reaction mixture was poured into water and extracted with ether, and the combined extracts were dried over anhydrous $MgSO_4$. Distillation gave 0.10 g (62%) of **4a**: bp 70–71 °C (0.5 mm); NMR ($CDCl_3$) δ 1.46 (d, J = 7 Hz, 3 H, $CHCH_3$), 2.35 (s, 3 H, o-CH_3), 3.62 (s, 3 H, OCH_3), 3.93 (q, J = 7 Hz, 1 H, $CHCH_3$), 7.0–7.4 (m, 4 H, aromatic H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.91. Found: C, 74.02; H, 7.97.

Irradiation of 4-Methylisochromene (1a) in Benzene. A solution of 1.0 g of **1a** in 500 mL of benzene was irradiated for 30 min. After the solvent had been removed at 0 °C (0.25 mm), the crude residue showed a band at 2125 cm^{-1} in the IR spectrum. Distillation of the crude reaction mixture gave 0.10 g of **6**, bp 40 °C (10 mm). The IR and NMR spectra of this material were identical with those of an authentic sample. An analytical-scale photolysis of **1a** in benzene, followed by addition of methanol to convert **3a** to **4a**, showed, by GC analysis using biphenyl as an internal standard, that 60% of **1a** had reacted to produce 22% of **6** and 22% of **4**.

Irradiation of 4-Methylisochromene (1a) in Methanol. A solution of 1.0 g (6.1 mmol) of **1a** in 250 mL of methanol was irradiated for 30 min. Distillation gave 0.30 g (28%) of **4a**, bp 72–73 °C (1.0 mm). The IR and NMR spectra of this material were identical with those of an authentic sample.

Irradiation of 3-Deuterio-4-methylisochromene (1b) in Methanol. A solution of 1.0 g of **1b** in 250 mL of methanol was irradiated for 1 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel, using 5% ether in hexane as eluant, to give 0.2 g of **4b**. The NMR spectrum of **4b** was identical with that of **4a** with the exception that the signal for the o-methyl group at δ 2.35 appeared as a triplet of lines of equal intensity (J_{H-D} = 2 Hz) that integrated for two protons.

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Registry No. **1a**, 32727-59-6; **1b**, 74082-01-2; **4a**, 74082-02-3; **4b**, 74082-03-4; **6**, 611-15-4; 3,3-dideuterio-4-isochromanone, 74096-70-1; 4-isochromanone, 20924-56-5; 2-(2-methylphenyl)propanoic acid, 62835-95-4.

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Halogenated Ketenes. 35. Cycloadditions of Halogenated Ketenes and Tetramethoxyethylene. Semisquaric Acid Derivatives

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The (2 + 2) cycloaddition of the electron-rich tetraalkoxyethylenes with some aldoketenes has been described by Bellus[1,2] as an intermediate step in the synthesis of squaric acid and 2-substituted semisquaric acid derivatives. We have recently reported on the cycloaddition of some tetraalkoxyethylenes with trimethylsilylketene to yield the tetraalkoxy-2-(trimethylsilyl)cyclobutanones which undergo acid-catalyzed hydrolysis to give semisquaric acid.[3] We now wish to report the cycloaddition of methylchloro-, dichloro-, and phenylchloroketenes with tetramethoxyethylene to yield the 2-chlorotetramethoxycyclobutanones. Hydrolysis of these cycloadducts results in ring cleavage to yield acyclic products. However, reduction of the 2-chlorotetramethoxycyclobutanones to the cyclobutanols and hydrolysis yield 2-substituted semisquaric acid derivatives.

This procedure involves the in situ generation of the ketene by the triethylamine dehydrohalogenation of α-chloropropionyl chloride, dichloroacetyl chloride or α-chlorophenylacetyl chloride in the presence of tetramethoxyethylene to produce the cyclobutanone in high yields (Scheme I).

The cycloaddition produces 2-substituted 2-chloro-3,3,4,4-tetramethoxycyclobutanones (**1a–c**) in high yields, which is consistent with yields (>80%) reported for the cycloaddition of tetraalkoxyethylene with aldoketenes.[1,2]

The adducts **1a** and **1b** are liquids which could be vacuum distilled whereas **1c** is a solid and was purified by sublimation. The infrared absorption spectra for the 2-halocyclobutanones revealed the carbonyl bands at 1800–1815 cm^{-1}.

The NMR spectrum of 2-methyl-2-chloro-3,3,4,4-tetramethoxycyclobutanone (**1a**) revealed a multiplet, δ 3.45–3.60, representing the 12 protons (4-OCH_3). This multiplet is expected since each set of protons on the four methoxy groups are nonequivalent. The NMR spectrum of 2,2-dichloro-3,3,4,4-tetramethoxycyclobutanone (**1b**) revealed two peaks, δ 3.45 (2-OCH_3) and 3.55 (2-OCH_3). In the case of **1c**, 2-chloro-2-phenyl-3,3,4,4-tetramethoxycyclobutanone, the NMR spectrum had a multiplet, δ 3.35 (3-OCH_3), and a singlet at δ 2.98 (1-OCH_3). The chemical shift of the C(3)-methoxy protons cis to the phenyl is shifted upfield due to the shielding effect of the benzene ring.

It was reported that the cycloadducts of tetraalkoxyethylene and aldoketenes could be hydrolyzed to squaric acid or semisquaric acid by 18% HCl. It is apparent that the cycloadducts of tetramethoxyethylene and disubstituted ketenes reported in this paper cannot be hydrolyzed to semisquaric acid derivatives because of the lack of an enolizable hydrogen. However, hydrolysis of these cycloaddition products could lead to cyclobutanediones or ring-opened acyclic products. Hydrolysis of the dichloro

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(4) Dao, H.; Hopkinson, A. C.; Ruff, E. L. *Tetrahedron Lett.* **1978**, 1413.

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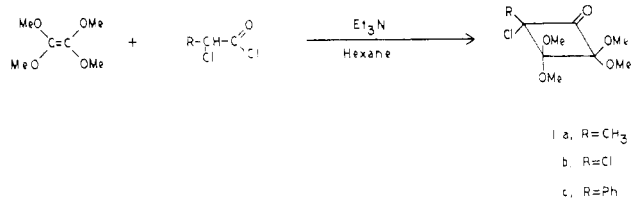
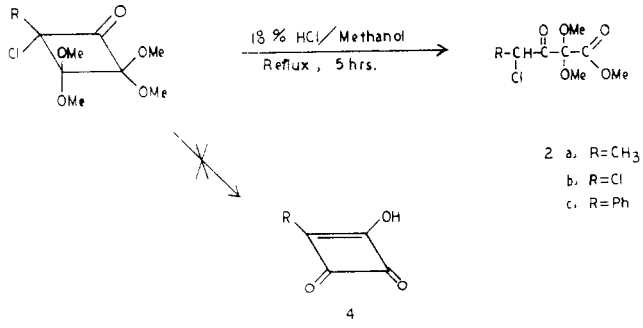
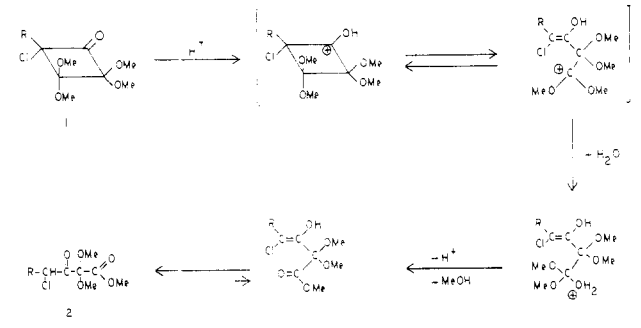
Scheme I



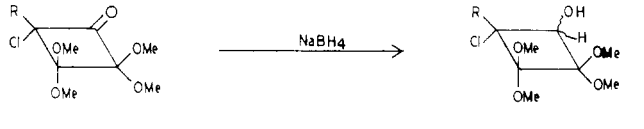
Scheme II



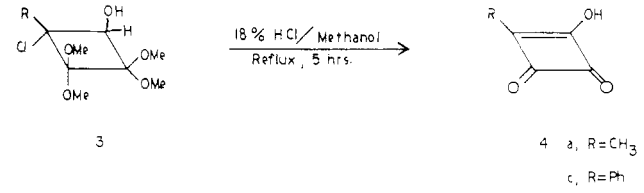
Scheme III



Scheme IV



Scheme V



adduct **1b** resulted in ring opening to the acyclic keto ester **2b** (Scheme II). Treatment of **1a** and **1c** with 18% HCl in methanol and heat also yielded quantitative amounts of **2a** and **2c**. Only small amounts of the corresponding acyclic keto esters were reported from the aldoketene cycloadducts with tetraalkoxyethylenes.[1,2]

A mechanism is proposed for this acid-catalyzed ring-opening reaction as illustrated in Scheme III. This mechanism involves the protonation of the cyclobutanone at the carbonyl oxygen and ring opening to form the enol carbonium ion, followed by nucleophilic attack of water with the subsequent loss of a proton and methanol to yield the enol ester. Tautomerization of the enol ester results in the formation of the keto ester.

The presence of an α-hydrogen in the cycloaddition product is necessary for hydrolysis to semisquaric acid derivatives. The α-hydrogen allows for the formation of an endocyclic double bond via enolization. The driving force for the formation of the semisquaric acid derivatives is then the conjugation of this double bond with the carbonyl groups.

The sodium borohydride reduction of the 2-substituted 2-chloro-3,3,4,4-tetramethoxycyclobutanones to the 2-chlorotetramethoxycyclobutanols occurs smoothly and quantitatively. The reduction of **1a,c** to **3a,c** (Scheme IV) produced an equal mixture of cis and trans isomers as evidenced by NMR.

The hydrolysis of **3a,c** resulted in the formation of the semisquaric acids **4a,c** (Scheme V). Hydrolysis of **3b** resulted in the formation of an unidentifiable brown substance.

Reduction of the cyclobutanone provides a ring hydrogen vicinal to the chlorine atom and allows the elimination of HCl. The formation of this endocyclic double bond is a prerequisite for hydrolysis to the cyclobutenedione as mentioned above.

In summary, we have shown that tetramethoxyethylene undergoes cycloaddition with chloroketenes in high yields to form tetramethoxycyclobutanones which undergo acid-catalyzed hydrolysis to ring-opened acyclic products, β-keto esters. Reduction of the cyclobutanones results in cyclobutanols which are hydrolyzable to semisquaric acid derivatives.

Experimental Section

Proton NMR spectra were recorded on a Perkin-Elmer R-24B NMR spectrometer employing CCl_4 as the solvent and tetramethylsilane or chloroform as the internal standard. VPC was performed on a Perkin-Elmer Model 3920-B gas chromatograph with a 4 ft × $^1/_4$ in. column packed with 10% QF-1 on acid-washed Chromosorb W(80–100) support. The infrared spectra were obtained on a Perkin-Elmer Model 621 grating infrared spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double-focusing spectrometer.

Hexane and triethylamine were dried and purified by distillation from sodium-potassium alloy prior to use. Dichloroacetyl chloride and α-chloropropionyl chloride were prepared from the corresponding acid and thionyl chloride. α-Chlorophenylacetyl chloride was purchased from Aldrich Chemical Co., Inc. Tetramethoxyethylene was prepared from formic acid, acetic anhydride, trimethyl orthoformate, and *p*-chlorophenol according to a literature procedure.[5] An improved yield was obtained by distilling the (*p*-chlorophenoxy)dimethoxymethane at a lower temperature, 65 °C (0.25 mm). Analytical samples were purified as a matter of routine by VPC methods.

General Procedure for the in Situ Cycloaddition of Chloroketenes with Tetramethoxyethylene. A solution of freshly distilled acid halide in 50 mL of dry hexane was added over 1 h to a stirred, refluxing mixture of 0.025 mol of tetramethoxyethylene and 0.0275 mol of triethylamine in 150 mL of dry hexane under a nitrogen atmosphere. After the addition was complete, the mixture was stirred for 4 h at reflux, and then stirring was continued overnight at room temperature. The amine salt was removed by filtration, and the filtrate was concentrated on a rotary evaporator. The residue was vacuum distilled to yield the cycloadduct.[6] There was no evidence of any acyclic products or vinyl esters in these reactions.

2-Chloro-2-methyl-3,3,4,4-tetramethoxycyclobutanone (1a). This cycloadduct distilled at 47–48 °C (0.025 mm) to give a yield of 4.77 g (80%): IR 1800 cm^{-1} (neat); NMR δ 1.75 (s, 3 H), 3.45–3.60 (m, 12 H); mass spectrum, *m/e* 238 (M).

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Anal. Calcd for $C_9H_{15}ClO_5$: C, 45.28; H, 6.29. Found: C, 44.92; H, 6.28.

2,2-Dichloro-3,3,4,4-tetramethoxycyclobutanone (1b). This adduct distilled at 57–58 °C (0.025 mm) to yield 5.48 g (85%) of product: IR 1815 cm^{-1} (neat); NMR δ 3.45 (s, 6 H), 3.55 (s, 6 H); mass spectrum, m/e (no M) 230 (M – 28).

Anal. Calcd for $C_8H_{12}Cl_2O_5$: C, 37.06; H, 4.63. Found: C, 36.81; H, 4.62.

2-Chloro-2-phenyl-3,3,4,4-tetramethoxycyclobutanone (1c). This cyclobutanone was produced as a white solid: mp 117–118 °C; 6.08 g (80%); IR 1805 cm^{-1} (CCl_4); NMR δ 2.98 (s, 3 H), 3.35 (m, 9 H), 7.08 (m, 5 H); mass spectrum, m/e 300 (M).

Anal. Calcd for $C_{14}H_{17}ClO_5$: C, 55.90; H, 5.65. Found: C, 55.92; H, 5.55.

Typical Procedure for the Hydrolysis of the 2-Chloro-3,3,4,4-tetramethoxycyclobutanones. A 1.0-g portion of the cycloadduct 1 was stirred at reflux for 5 h in 15 mL of 18% methanolic HCl solution. The solvent was then removed under vacuum, leaving the keto ester.

Methyl 4-Chloro-2,2-dimethoxy-3-oxopentanoate (2a). A 1.0-g (4.2 mmol) portion of 1a was treated with the acid/methanol solution to yield a quantitative amount of the keto ester **2a**: IR 1770, 1750 cm^{-1} (neat); NMR δ 1.50 (d, 3 H, J = 5 Hz), 3.25 (s, 3 H), 3.40 (s, 3 H), 3.70 (s, 3 H), 4.75 (q, 1 H, J = 5 Hz); mass spectrum, m/e (no M) 193 (M – 31).

Anal. Calcd for $C_8H_{13}ClO_5$: C, 42.76; H, 5.79. Found: C, 42.70; H, 5.78.

Methyl 4,4-Dichloro-2,2-dimethoxy-3-oxobutanoate (2b). A 1.0-g (3.8 mmol) portion of **1b** was treated with the acid/methanol solution to give a quantitative yield of the keto ester **2b**: IR 1780, 1770 cm^{-1} (neat); NMR δ 3.35 (s, 6 H), 3.80 (s, 3 H), 6.45 (s, 1 H); mass spectrum, m/e (no M) 213 (M – 31).

Anal. Calcd for $C_7H_{10}Cl_2O_5$: C, 34.28; H, 4.08. Found: C, 34.46; H, 4.14.

Methyl 4-Chloro-2,2-dimethoxy-3-oxo-4-phenylbutanoate (2c). A 1.0-g (3.3 mmol) portion of **1c** was treated with the acid/methanol solution to give a quantitative amount of the ester **2c**: IR 1770, 1750 cm^{-1} (neat); NMR δ 3.25 (s, 3 H), 3.40 (s, 3 H), 3.62 (s, 3 H), 5.92 (s, 1 H), 7.30 (m, 5 H); mass spectrum, m/e (no M) 255 (M – 31).

Anal. Calcd for $C_{13}H_{15}ClO_5$: C, 54.45; H, 5.23. Found: C, 54.25; H, 5.31.

Typical Procedure for the Sodium Borohydride Reduction of the Cyclobutanones. To a stirred solution of 1.0 g of the cycloadduct 1 in 10 mL of anhydrous isopropyl alcohol was slowly added a 20% excess of sodium borohydride. The mixture was stirred at room temperature overnight. The alcohol was evaporated under vacuum and the residue shaken with 10 mL of 10% HCl. Extraction with two 10-mL portions of CCl_4, drying of the extract over $MgSO_4$, and evaporation of the solvent resulted in the solid alcohol. The alcohol was purified by sublimation.

2-Chloro-2-methyl-3,3,4,4-tetramethoxycyclobutanol (3a). The reduction of 1a quantitatively produced **3a**, a white solid, which was isolated as a mixture of isomers melting at 47–51 °C: IR 3550 cm^{-1} (CCl_4); NMR δ 1.70 (s, 3 H), 2.68 (br s, 1 H), 3.3–3.45 (m, 12 H), 3.72, 3.88 (s, s, 1 H); mass spectrum, m/e 240 (M).

Anal. Calcd for $C_9H_{17}ClO_5$: C, 44.91; H, 7.06. Found: C, 44.65; H, 7.19.

2,2-Dichloro-3,3,4,4-tetramethoxycyclobutanol (3b). The reduction of **2a** also quantitatively produced **3a** as a white solid: mp 61–62 °C; IR 3550 cm^{-1} (CCl_4); NMR δ 3.40–3.55 (m, 12 H), 3.8 (br s, 1 H), 4.10 (s, 1 H); mass spectrum, m/e 260 (M).

Anal. Calcd for $C_8H_{14}Cl_2O_5$: C, 36.80; H, 5.40. Found: C, 36.87; H, 5.61.

2-Chloro-2-phenyl-3,3,4,4-tetramethoxycyclobutanol (3c). The reduction of 1c quantitaviely produced **3c**, a white solid, which was isolated as an equal mixture of isomers: mp 71–74 °C; IR 3550 cm^{-1} (CCl_4); NMR δ 3.05, 3.35 (s, s, 1 H), 3.15 (s, 3 H), 3.25 (s, 3 H), 3.40 (s, 6 H), 4.3 (br s, 1 H), 6.9–7.4 (m, 5 H); mass spectrum, m/e (no M) 284 (M – 18).

Anal. Calcd for $C_{14}H_{19}ClO_5$: C, 55.55; H, 6.33. Found: C, 55.65; H, 6.18.

Procedure for Conversion of Cyclobutanols to 2-Substituted Semisquaric Acids. A 1.0-g portion of the cyclobutanol was heated at reflux in 15 mL of 18% methanolic HCl. The solvent was removed by evaporation, resulting in the isolation of the semisquaric acid. No further purification was necessary.

2-Methylsemisquaric Acid (1-Hydroxy-2-methyl-1-cyclobutene-3,4-dione, 4a). Hydrolysis of 1.0 g of the cyclobutanol **3a** yielded a quantitative amount of the acid derivative **4a**: mp 162–164 °C dec (lit.[7] mp 162–164 °C dec); the IR and NMR were identical with those found in the literature.

2-Phenylsemisquaric Acid (1-Hydroxy-2-phenyl-1-cyclobutene-3,4-dione, 4c). Hydrolysis of 1.0 g of the phenyl-substituted cyclobutanol **3c** also yielded a quantitative amount of the solid acid **4c**: mp 208–211 °C (lit.[8] mp 208–211 °C).

Acknowledgment. The authors express appreciation to the Robert A. Welch Foundation and to the North Texas State University Faculty Research for support of this investigation.

Registry No. 1a, 74176-08-2; **1b**, 74176-09-3; **1c**, 74176-10-6; **2a**, 74176-11-7; **2b**, 74176-12-8; **2c**, 74176-13-9; *cis*-**3a**, 74176-14-0; *trans*-**3a**, 74176-15-1; **3b**, 74176-16-2; *cis*-**3c**, 74176-17-3; *trans*-**3c**, 74176-18-4; **4a**, 29769-75-3; **4c**, 708-10-1; tetramethoxyethylene, 1069-12-1; α-chloropropionyl chloride, 7623-09-8; dichloroacetyl chloride, 79-36-7; α-chlorophenylacetyl chloride, 2912-62-1.

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Addition of Hydrohalogenic Acids to Alkenes in Aqueous–Organic, Two-Phase Systems in the Presence of Catalytic Amounts of Onium Salts

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In previous works[1,2] we reported that lipophilic quaternary ammonium and phosphonium salts show a high catalytic activity in reactions promoted by hydrohalogenic acids in aqueous–organic two-phase systems such as the conversion of alcohols to the corresponding halides[1] and the cleavage of ethers.[2] Recently quaternary ammonium salts were shown to extract hydrohalogenic acids from their aqueous solutions into low-polarity organic solvents.[3]

We here report that, under phase-transfer conditions, aqueous HCl, HBr, and HI are easily added to carbon–carbon double bonds according to Markovnikov's rule. Classically this reaction is carried on with gaseous hydrogen halides in peroxide-free polar solvents in the presence of radical scavengers.[4] The reaction can be much more advantageously accomplished by stirring at 115 °C (bath temperature) a heterogeneous mixture of the alkene (1 mol), the catalyst (0.1 mol), and the appropriate aqueous hydrohalogenic acid (3–15 mol) (see eq 1). Under these

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