Preparation and Reactions of Derivatives of Squaric Acid. Alkoxy-, Hydroxy-, and Aminocyclobutenediones[1]

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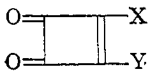
Abstract: Derivatives of squaric acid, 1,2-dihydroxycyclobutenedione (Ia), have been prepared and studied. 1,2-Dimethoxycyclobutenedione (Ib) was prepared from Ia. It is readily hydrolyzed to 1-hydroxy-2-methoxycyclobutenedione (Ic): with water $k_w = 1.2 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$; with hydroxide $k_b = 1.2 \times 10^{2}\ M^{-1}\ \text{sec}^{-1}$. Ic is further hydrolyzed to Ia: with water $k_w' \sim 2 \times 10^{-7}\ M^{-1}\ \text{sec}^{-1}$; with hydroxide $k_b' \sim 2 \times 10^{-1}\ M^{-1}\ \text{sec}^{-1}$. Compound Ib was also converted to 1,2-diethoxycyclobutenedione (Id), to 1-methoxy-2-aminocyclobutenedione (Ie), and to 1,2-diaminocyclobutenedione (If). In this set alkoxy compounds show λ_{max} *ca.* 250 mμ, hydroxy compounds λ_{max} *ca.* 265 mμ, and amino compounds λ_{max} *ca.* 270 mμ; hydroxy–alkoxy and amino–alkoxy compounds show double maxima. The hydroxyls are strongly acidic, the alkoxyl compounds behave like reactive esters, and the amino compounds behave like high-melting acidic amides.

Squaric acid[2] (Ia) and its dianion are members of a set of cyclic dibasic acids[3,4] $C_nO_nH_2$ (n = 4 squaric acid, n = 5 croconic acid, n = 6 rhodizonic acid) and of a set of the corresponding symmetrical aromatic dianions[3,4] $C_nO_n^{-2}$. Squaric acid, with four sp^2 ring carbon atoms, is related formally to the cyclobutadienes, and more directly to the so-called cyclobutadienoquinones, phenylcyclobutenedione,[5] diphenylcyclobutenedione,[6] dimethylcyclobutenediones,[7] and benzo- and naphthocyclobutenedione.[8]



Ia, X = Y = OH
Ib, X = Y = OCH_3
Ic, X = OH; Y = OCH_3
Id, X = Y = OC_2H_5
Ie, X = OCH_3; Y = NH_2
If, X = Y = NH_2

The chemistry of phenylcyclobutenedione has been studied in detail.[5b,c] It undergoes ring-opening reactions with basic reagents. It is converted by chlorine and bromine to the 2-chloro and 2-bromo derivatives; these are vinylogs of acyl halides and may be converted to the 2-hydroxy-, 2-methoxy-, and 2-aminophenylcyclobutenediones, which have strong acid, ester, and amide properties.[5b] Diphenylcyclobutenedione[6] appears to be less stable; it undergoes ring opening readily and is converted to diethyl α,α'-diphenylsuccinate, possibly *via* the valence tautomer, bisphenylketene.

Squaric acid (Ia) is a very strong acid, pK_2 = 2.2, within 0.7 pK unit of sulfuric acid.[2] Its dianion has high delocalization energy[3,6] comprising a stable, four-membered ring structure, and its complexes[3f] with divalent and trivalent metal cations have been characterized. It appeared of interest to prepare and study some covalent derivatives which could lack the stabilization of the dianion.

We now report the conversion of Ia to dimethoxycyclobutenedione (Ib) and to 1-hydroxy-2-methoxycyclobutenedione (Ic), the kinetics of hydrolysis of Ib to Ic and to Ia, and the conversion of Ib to diethoxycyclobutenedione (Id), to 1-amino-2-methoxycyclobutenedione (Ie), and to 1,2-diaminocyclobutenedione (If). While this work was in progress the preparation of dibutoxycyclobutenedione (I), X = Y = OC_4H_9, was reported.[9]

Results

Dimethoxycyclobutenedione, dimethyl squarate (Ib), was readily prepared (1) by treatment of Ia with diazomethane and (2) by treatment of the silver salt of Ia with methyl iodide. Compound Ib melts at 56° and shows detailed features in the infrared, C—H at 3.5, cyclobutenone[2] C=O at 5.55, conjugated C=C at 5.8 and 6.25, vinylic C—O at 8.2, and C—O at 9.65 μ. In contrast,[2] squaric acid (Ia) decomposes at *ca.* 293° and shows the C=O and C=C bands but no detail beyond 7 μ. In the ultraviolet, compound Ib shows a broad absorption band λ_{max} 246 mμ (log ϵ 4.32) in methanol, while compound Ia has λ_{max} 269 mμ (log ϵ 4.43) in water.

Compound Ib is stable in sealed tube or in a desiccator but is sensitive to moisture and is hydrolyzed. Its ultraviolet absorption band in water is initially very similar to that in methanol. With time, two maxima appear at 245 and 265 mμ, which prove to be characteristic of the half-ester Ic. Squaric acid, when stirred with methanol, dissolves with reaction forming a

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(1) We are pleased to acknowledge support of this work by National Science Foundation College Teachers Summer Research Grants GE3085 and 7569.

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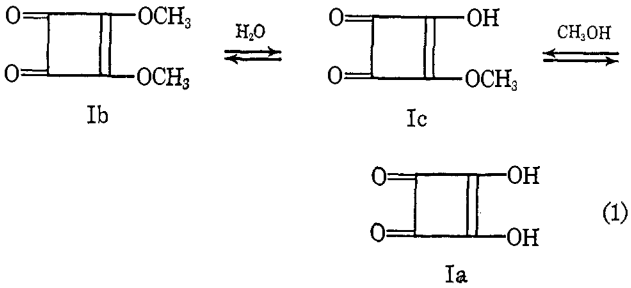
solution which is that of the monobasic acid Ic, as indicated by titration and by the ultraviolet spectrum, which is identical with that of the solution of diester Ib after standing in water, and with that of authentic Ic.



Ib Ic Ia (1)

The half-ester Ic was synthesized from Ia and methanol, mp 132–134°. It showed proper neutralization equivalent, elementary analysis, infrared bands similar to those of compound Ib, and, in addition, the hydrogen bonded acidic O—H, 3.9–4.4 μ. The two bands of compound Ic in water at 245 mμ (log ε 4.36) and 265 mμ (log ε 4.34) are related to those of Ib and Ia, respectively. In 3 *M* hydrochloric acid, compound Ic shows only the one band at 247 mμ (log ε 4.34). In mineral acid squaric acid itself also shows a shift of its absorption maximum from 269 to 246 mμ.

In preliminary experiments the kinetics of hydrolysis of 10^{-2} *M* Ib was followed in water without neutralization of the formed acid, the pH falling to about 2. This hydrolysis to Ic showed $k \sim 8.5 \times 10^{-5}$ sec^{-1}, and the hydrolysis of Ic to Ia, $k \sim 1 \times 10^{-5}$ sec^{-1}. Squaric acid was isolated as the product of hydrolysis. Studies were then carried out in the kinetics of hydrolysis of Ib to Ic in water as a function of pH and added sodium perchlorate. Some observed apparent first-order rate constants are listed in Table I.

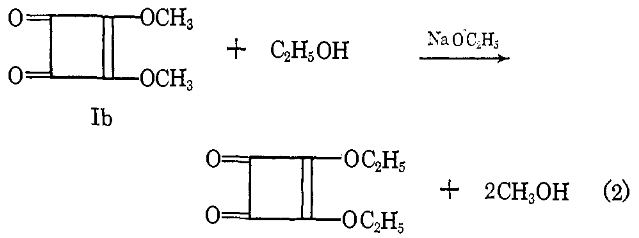
Table I. Effects of pH and Ionic Strength on the Hydrolysis of 5–10 × 10^{-3} *M* Dimethyl Squarate, 26°

$$\text{Ib} + H_2O \longrightarrow \text{Ic} + CH_3OH$$

pH	[NaClO$_4$], *M*	10^5k_{obsd}, sec^{-1}
4.0	. . .	7.0
5.0	. . .	6.9
5.0	0.1	6.7
5.0	0.5	5.1
5.0	1.0	3.2
6.0	1.0	3.4
7.0	. . .	6.5
8.0	. . .	17.6
8.5	. . .	43.0
9.0	. . .	140
9.0	0.1	136

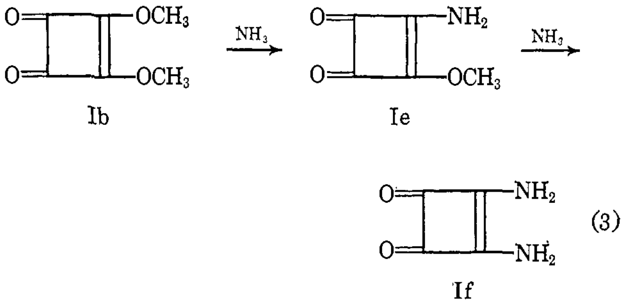
Some data were also obtained on the hydrolysis at pH 10–11 of 10^{-2} *M* Ic to Ia, compound Ic being prepared *in situ* from Ib. At pH 10.0, 10.5, and 11.0 the observed apparent first-order rate constants were 2.0, 11, and 19 × 10^{-5} sec^{-1}, respectively.

Compound Ib thus being very reactive in alkali, some syntheses were carried out. Treatment with ethanol in the presence of a catalytic quantity of sodium ethoxide led readily to diethoxycyclobutenedione (Id), a liquid with infrared and ultraviolet spectral properties quite similar to those of Ib. The broad ultraviolet band at 253 mμ (log ε 4.29), in water, changed on standing to a band with two maxima, 245 mμ (log ε 4.28) and 265 mμ (log ε 4.27), presumably characteristic of the corresponding half-ester I (X = OH; Y = OC_2H_5). This spectrum persisted but in this case no attempt was made to isolate or prepare the half-ester. The kinetics of hydrolysis of $\sim 10^{-2}$ *M* Id were examined briefly. At pH 6.0, 9.0, and 9.55 the observed first-order rate constants were 1.4, 23, and 72 × 10^{-5} sec^{-1}, respectively.



Ib (2)

Treatment of Ib with ammonia led to replacement of the methoxyl groups by amino. The monoamino compound Ie is very slightly soluble in ether (*ca.* 0.02%) and treatment of a solution of Ib in ether with gaseous ammonia led to precipitation of Ie in high yield. This does not show a melting point and decomposes at about 200°, while Ic, the monohydroxy ester, melts at 132–134°. The infrared spectrum of Ie shows acidic amide N-H bands at 3.0 and 3.2 μ, bands typical of C=O and C=C in cyclobutenones, and much detail between 7 and 11 μ. Its ultraviolet spectrum in water shows two maxima, at 250 mμ (log ε 4.35) and at 264 mμ (log ε 4.35).



Ib Ie If (3)

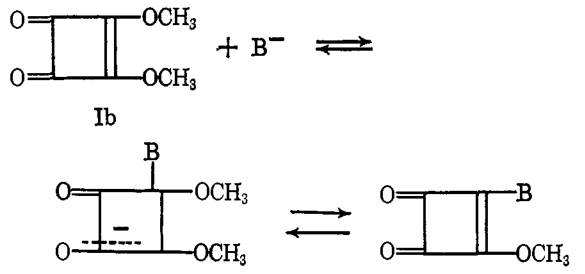
The ammonolysis in ether led also to formation of the diamino compound If in low yield, but this was better prepared by treatment of Ib with a solution of gaseous ammonia in methanol, in which the monoamino compound Ie is soluble. Compound If may also be prepared by treatment of solutions of Ib in ether or in methanol with concentrated ammonium hydroxide. Compound If is a yellow solid which darkens but does not melt up to 350°. It shows acidic amide N-H bands at 3.0 and 3.2 μ, C=O and C=C bands much like those of Ia and Ib, but, like squaric acid itself, no bands between 7.8 and 13.8 μ. A solution in water shows a low-intensity, long wavelength band, $\lambda_{\max}$ 363 mμ (log ε 3.04), and a broad high-intensity band, $\lambda_{\max}$ 275 mμ (log ε 4.42), the latter being similar to that of squaric acid itself but at slightly longer wavelength.

Discussion

The ready conversion of Ia to Ib by diazomethane was accompanied by formation of a yellow by-product, possibly due to ring enlargement. Treatment of the homolog, croconic acid, with diazomethane has led to the corresponding dimethyl ester and, in addition, to trimethoxybenzoquinone.[4a] Analogous ring enlargement of Ib might lead to interesting derivatives of cyclopentadienone. Synthesis of Ib from the silver salt of Ia subsequently proved effective and convenient.

The parent acid Ia shows infrared bands due to hydrogen bonded O—H, C=O, and C=C, but no further detail. Its anion is highly stabilized and shows essentially no bands due to localized structure. The diester Ib shows localized structure and high chemical reactivity. Although squaric acid Ia is a very strong acid, it is apparently protonated in strong mineral acid, its ultraviolet absorption maximum shifting from about 269 mμ, which appears to be characteristic of the anion character of both Ia and Ic, to 246 mμ, which is characteristic of the ester of both Ib and Ic. The half-acid monoester Ic, with absorption at both 245 and 265 mμ in water, also shows repression of its ionization in strong acid, and its ultraviolet absorption in acid is similar to that of the diester in neutral medium.

Dimethoxycyclobutenedione (Ib) shows high reactivity toward water and basic reagents without opening the four-membered ring, unlike diphenylcyclobutenedione[6] and, to a lesser extent, phenylcyclobutenedione.[5] Reaction apparently occurs by attack at the vinylogous ester position.



(4)

Reaction with water leads first to the half-acid Ic, which is also prepared readily from squaric acid and methanol. Hydrolysis of Ib to Ic show little if any acid catalysis, being about 20% more rapid at pH ~2.5 than at 5, and having about the same rate at pH 5 and 7. The reaction shows a small, negative salt effect, proceeding at pH 5 at half the rate in the presence of 1 *M* sodium perchlorate as in its absence. This indicates that a solvolytic dissociation at the methyl–oxygen bond is not occurring, which might have been possible because of the acid strength of Ia. The reaction was strongly catalyzed by base, being 21 times more rapid at pH 9 than at 7 (half-life 8.5 min). The observed apparent first-order rates appear to result from concurrent bimolecular reactions of ester with water and with hydroxide.

$$k_{\text{obsd}} = k_{\text{w}}\,(\text{H}_2\text{O}) + k_{\text{b}}\,(\text{OH}^-)$$

$$k_{\text{w}} = 1.2 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$$

$$k_{\text{b}} = 1.2 \times 10^{2}\ M^{-1}\ \text{sec}^{-1}$$

At pH <7 the reaction occurs largely with water and is relatively slow, while at pH >7 it occurs largely with hydroxide. The reactivity of hydroxide is 10^8 greater than that of water, a factor more consistent with that of their relative reactivity[10] toward the sp^2 carbonyl carbon of an ester than toward an sp^3 aliphatic carbon. The reactivity toward hydroxide is about 10^{-2} as great as the reactivity of dimethyl oxalate[11] and 10^3 as great as the reactivity of methyl acetate.

The hydrolysis of the negatively charged monoester Ic to the dianion Ia was examined briefly in alkali and found to be fairly rapid. A substantial part of the hydrolysis of Ic appears due to hydroxide, the reaction proceeding almost ten times more rapidly at pH 11 than at pH 10. If it is entirely due to hydroxide at this alkalinity, the rate constant k_b' is about 2×10^{-1} M^{-1} sec^{-1}. Hydrolysis of the diester Ib to Ic at pH 10 is estimated to be 7×10^2 that of Ic to Ia. This ratio is less than that of the two rate constants in the hydrolysis of dimethyl oxalate[12] which is about 2×10^4. The difference in these ratios may reflect the unusual resonance stabilization of the dianion of Ia. Hydrolysis of Ic in acid, pH ~2 was about half as fast as at pH 10, $k_w \sim 2 \times 10^{-7}\ M^{-1}$ sec^{-1}. This rate constant, when corrected by a statistical factor of 2, indicates a reactivity of Ic, as acid–ester or as anion–ester or both, toward water which is about half that of the diester Ib toward water.

The capacity of Ib to react readily with a basic reagent without opening the four-membered ring did not depend upon formation of a stabilized mono- or dianion. Reaction with ethanol in the presence of sodium ethoxide led readily to the diethyl ester Id in high yield (eq 2), presumably by successive reactions according to eq 4. Many esters, both from monohydroxy and polyhydroxy alcohols may be accessible through such ester interchange. Id was hydrolyzed at about one-fifth the rate of the dimethyl ester at pH 6 and 9. Its spectral properties were similar to those of the dimethyl ester.

Interesting synthetic possibilities with nitrogen bases are indicated in the reactions of Ib with ammonia, which lead readily to the monoamide–monoester Ie and the diamide If. The monoamide may be quite strongly hydrogen bonded, decomposing at 200°; its ultraviolet spectrum showed a double peak, much like that of the monoacid Ic. The diamide If is a highly insoluble, infusible, yellow material, presumably strongly hydrogen bonded. Its infrared spectrum is much like that of squaric acid itself, Ia. It is slightly acidic and dissolves more readily in 0.5 *N* sodium hydroxide than in water, leading presumably to delocalized anionic structures which are more highly absorbing in the visible. The yellow color of its aqueous solution is discharged on acidification, indicating that the color in neutral solution may be due to monoanion.

The reactions of dimethyl squarate (Ib) with water, alkali, alcohol, and ammonia are similar to those characteristic of attack at the carbonyl group in esters of strong carboxylic acids, Ib being, in a way, a cyclic vinylog of dimethyl oxalate. It remains to be seen whether, under appropriate conditions, compound Ib may also act as an alkylating agent *via* S_N2 reactions at the alkyl–oxygen carbon atoms.

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Experimental Section

Elemental and functional group analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and by Dr. Carol Fitz, Needham Heights, Mass. Melting points are uncorrected. Infrared absorption spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer, optical densities on a Beckman DU-2 spectrophotometer.

Squaric Acid (Ia). 1,2-Dichloro-3,3,4,4-tetrafluorocyclobutene (Penninsular Chemical Research Co., Inc., 200 g, 1.02 moles) in 200 ml of ethanol was added with stirring and intermittent cooling over a period of 4 hr to 200 g (3.6 moles) of potassium hydroxide in 450 ml of 95% ethanol. The mixture was diluted and washed with water, dried, and distilled, leading to 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene, 204 g (0.80 mole, 79% yield), bp 138° (11 mm), $n^{25}\text{D}$ 1.4278. This compound (100 g, 0.39 mole) was heated with 200 ml of concentrated hydrochloric acid[3d] for about 3 hr, concentrated, and decanted. The solid residues were crystallized from water and washed with acetone and ether, yielding compound Ia, 38 g (0.34 mole, 86% yield); neut equiv 56.9 (calculated for $C_4O_4H_2$ 57.0); λ_{max} 269 $m\mu$ (log ϵ 4.43) in water.

Dimethyl Squarate Dimethoxycyclobutenedione (Ib). 1. A suspension of 5.7 g (0.050 mole) of Ia in 125 ml of ether was cooled and stirred, and into it was distilled ethereal diazomethane, prepared by addition of 65 g (0.30 mole) of N-methyl-N-nitroso-*p*-toluenesulfonamide (Diazald, Aldrich) in 400 ml of ether to 15 g of potassium hydroxide in 24 ml of water and 76 ml of ethanol. The reaction was rapid, the squaric acid largely dissolved, and a small insoluble enolic orange residue (0.25 g) remained. The solution was warmed briefly and concentrated at room temperature, leading to compound Ib, 4.7 g (0.033 mole, 66% yield), mp 55° from ether.

2. A solution of 5.46 g (0.048 mole) of squaric acid in 250 ml of water was neutralized with 1 *N* sodium hydroxide and treated with a solution of 16.3 g (0.096 mole) of silver nitrate in 100 ml of water. The light yellow precipitate of disilver squarate was filtered and washed with water, acetone, and ether. Concentration of the filtrate led to additional silver squarate, which was soluble to the extent of about 0.4%. The dried silver salt was boiled for 2 hr in 25 ml of methyl iodide and 50 ml of ether and shaken for 2 days. The mixture was filtered, the residue was washed with ether, and the ether was concentrated, leading to Ib, 5.45 g (0.038 mole, 79% yield), mp 56.7–58.0°, fluffy white crystals, soluble in methanol and benzene. Infrared absorption bands (potassium bromide pellet) were at 3.5, 5.55, 5.8, 6.3, 6.75, 7.1, 7.35, 8.2, 8.75, 9.2, 9.65, 10.65, 10.75, and 12 μ.

Anal. Calcd for $C_6H_6O_4$: C, 50.71; H, 4.25; CH_3O, 43.68. Found: C, 50.92; H, 4.13; CH_3O, 43.47.

1-Hydroxy-2-methoxycyclobutenedione (Ic). Squaric acid (Ia) (3.50 g, 0.0307 mole) was boiled in 100 ml of methanol for 3 hr. The solution was concentrated under vacuum to contant weight of powdery residue, 3.79 g, neut equiv 104 (calculated for Ic 128) indicating the presence of Ia. The powder was taken up in hot isopropyl ether–methanol, filtered, and diluted with hot isopropyl ether. Compound Ic was collected by centrifuge, neut equiv 128, mp 132–134°, with white solid forming. Infrared absorption bands, potassium bromide pellet, were at 3.36, 4.1–4.3, 5.5, 5.8, 6.3–6.4, 6.75, 7.05, 7.25, 8.2, 9.35, 9.6, 10.8, 11.0–11.2, 12.0, 12.1, and 12.65 μ. Broad ultraviolet absorption bands were at 245 $m\mu$ (log ϵ 4.36) and 265 $m\mu$ (log ϵ 4.34) in water; these bands persisting with little change in intensity on storage of the solution.

Anal. Calcd for $C_5H_4O_4$: C, 46.90; H, 3.14; CH_3O, 24.23. Found: C, 47.1; H, 3.3; CH_3O, 24.0.

Hydrolysis of Ib to Ic and Ia. A solution of 0.370 g (2.50 mmoles) of Ib in 250 ml of water (1.00×10^{-2} *M*) was prepared and the hydrolysis was followed both by titration of aliquots with a Radiometer titrator set at pH 6 and by change in the ultraviolet absorption at 245, 265, and 269 $m\mu$. The hydrolysis took place at pH 2.5–2.0, the acidity due to formation of Ic. The hydrolysis showed first-order kinetics at 25°, over 87% hydrolysis of the first ester group, half-life 137 min, $k = 8.5 \times 10^{-5}$ sec^{-1}, leading to the absorption maxima at 245 $m\mu$ (log ϵ 4.34) and 265 $m\mu$ (log ϵ 4.33). After 36 hr the second ester group was 70% hydrolyzed, indicating a first-order rate constant for hydrolysis of Ic to Ia of about 1×10^{-5} sec^{-1} at pH <2.0. After 8 days, the remainder of the solution was concentrated to dryness, and the residue was washed with acetone and ether and dried, neut equiv 57.9 (calculated for Ia 57.0). The infrared and ultraviolet spectra were identical with those of Ia.

Rates of Hydrolysis. A weighed quantity of dimethyl squarate was added to a 20-ml portion of distilled water stirred magnetically under nitrogen, maintained at 26.0°, and at constant pH by a Radiometer TTT1B titrator which delivered 0.1 *N* sodium hydroxide from an Aminco automatic pipet. The volume of added alkali was read as a function of time. Linear plots of log of ester concentration against time were obtained and from them the observed first-order constants were calculated.

Diethyl Squarate (Id). Dimethyl squarate (1.68 g, 0.0118 mole) in 10 ml of absolute ethanol was boiled under reflux for 3 hr in 25 ml of ethanol containing a small amount of sodium ethoxide. The solution was concentrated, the residue was extracted with ether, and the extract was concentrated and distilled, leading to diethoxycyclobutenedione (Ic), bp 89–91° (0.4 mmole), $n^{25}\text{D}$ 1.5000, 1.54 g (0.0091 mole, 77% yield). Infrared absorption bands (film) were at 3.4, 5.6, 5.8, 6.3, 6.8, 7.1, 7.3, 7.55, 7.8, 8.35, 8.75, 9.2–9.3, 9.8, 10.1, 11.45, 11.7, 12.25, and 12 5 μ.

Anal. Calcd for $C_8H_{10}O_4$: C, 56.48; H, 5.92; C_2H_5O, 52.95. Found: C, 56.16; H, 6.27; C_2H_5O, 52.40.

1-Amino-2-methoxycyclobutenedione (Ie). Compound Ib (0.303 g, 2.12 mmoles) was dissolved in 50 ml of dry ether, cooled to 0°, and treated with ammonia gas until precipitation was completed. The mixture was boiled gently, the ether was decanted, and the solid was washed with ether, dried, and crystallized from acetone–petroleum ether, yielding compound Ie, 0.201 g (1.59 mmoles, 75% yield), a white solid, darkens 170°, dec ~202°. Infrared absorption bands, potassium bromide pellet, were at 3.0, 3.2, 5.5, 5.9, 6.1, 6.45, 6.75, 7.15, 7.95, 8.4, 8.8, 9.55, 9.9, 10.85, and 12.8 μ.

Anal. Calcd for $C_5H_5NO_3$: C, 47.27; H, 3.97; N, 11.03; CH_3O, 24.42. Found: C, 47.5; H, 4.0; N, 11.1; CH_3O, 24.5.

A small, yellow residue which had not dissolved in the acetone in the crystallization of Ie proved to be the diamino compound If, 0.024 g (0.21 mmole, 10% yield).

Diaminocyclobutenedione (If). Compound Ib (0.300 g, 2.11 mmoles) in 20 ml of dry methanol was added with stirring at 0° to a saturated solution of gaseous ammonia in 50 ml of dry methanol. The yellow diamino compound If soon precipitated. The mixture was warmed for 1 hr, the supernatant was decanted, and the solid was washed with acetone and ether and dried, yielding 0.205 g (1.83 mmoles, 87% yield). This compound is very slightly soluble in water ($\sim 10^{-3}$ *M*) and in hot methanol, from which it precipitates on cooling. It does not melt, turning dark over 250°, with no noticeable gas evolution when heated to 350°. Infrared absorption bands, potassium bromide pellet, were at 3.02, 3.2, 5.5, 6.03, 6.2, 6.45, 6.7, 7.3, 7.8, and 13.8 μ. In the ultraviolet there was a broad absorption, λ_{max} 275 $m\mu$ (log ϵ 4.42), and a weaker band, λ_{max} 363 $m\mu$ (log ϵ 3.04).

Anal. Calcd for $C_4H_4N_2O_2$: C, 42.86; H, 3.59; N, 25.00. Found: C, 42.97; H, 3.66; N, 24.99.