of the adjacent alkoxy group at C(11).[29] Conversely, quaternization methods requiring carbonium ion character at C(12) were unsuccessful, possibly due to the inductive nature of the C(11) alkoxy group.[30] The quaternization problem was solved by a two-part sequence which we feel should prove useful in other hindered and sensitive cases of this type. Ozonolysis of **19** (MeOH–CH_2Cl_2, −78 °C), followed by immediate reduction of the hydroperoxide ($P(OCH_3)_3$, −78 °C), produced the ketone **20** (mp 109–110 °C) in near quantitative yield. Addition of **20** to (*Z*)-[2-ethoxyvinyl]lithium (50 equiv, THF, −35 to −30 °C, 0.5 h), followed by acid hydrolysis (1:2 20% H_2SO_4(aq)–THF) gave the α,β-unsaturated aldehyde **21** in 50% yield.[31] Reduction with DIBAH (CH_2Cl_2, 0 °C, 95%) yielded the allylic alcohol **22** (mp 122–123 °C). By means of Murahashi's γ-alkylation procedure (CuI, MeLi, n-$Bu_3P^+N(CH_3)PhI^-$, THF), the allylic alcohol **22** was converted exclusively to the desired epimer **23** in 50% yield.[32] Transformation of **23** to mutilin (**2**) was carried out in three steps. Removal of the benzyl group (Li, NH_3(liq)), followed by oxidation of **24** (PCC, CH_2Cl_2) produced the ketone **25**. Finally, deprotection of **25** (3% HCl–EtOH, 25 °C) gave (±)-mutilin (**2**) as a white crystalline solid (mp 187–189.5 °C, CH_2Cl_2/hexane, 80% overall yield), spectroscopically indistinguishable (IR, ^1H NMR, ^{13}C NMR, MS) from the naturally derived material.[4,5] Mutilin was converted to pleuromutilin (**1**) by diesterification ($AcOCH_2COOH$, MsCl, DMAP, pyridine–THF, 25 °C)[33] and mild hydrolysis (5% KOH–MeOH, 25 °C, 12 h).[34]

Acknowledgment. The author is indebted to the late Professor R. B. Woodward for his guidance and support (National Science Foundation Grant CHE 78-25699), to Professor Y. Kishi for valuable advice and encouragement, and to Professor D. Arigoni for generous assistance and a gift of pleuromutilin.

Registry No. 1, 80924-94-3; **2**, 80924-95-4; **3**, 73192-77-5; **4**, 80878-23-5; **5**, 80878-24-6; **5**, α,β-unsaturated aldehyde derivative, 80878-25-7; **6**, 80890-19-3; **7**, 80890-20-6; **7**, bridged aldol product, 80890-21-7; **7**, endo olefin product, 80906-62-3; **8**, 80951-30-0; **9**, 80890-22-8; **10**, 80878-26-8; **11a**, 80878-27-9; **11b**, 80878-28-0; **12**, 80890-23-9; **13**, 80878-29-1; **14**, 80878-30-4; **15**, 80878-31-5; **16**, 80878-32-6; **17**, 80878-33-7; **18**, 80924-96-5; **19**, 80878-34-8; **19**, hydroperoxide derivative, 80878-35-9; **20**, 80878-36-0; **21**, 80878-37-1; **22**, 80878-38-2; **23**, 80878-39-3; **24**, 80878-40-6; **25**, 80878-41-7; i, 80878-42-8; ii, 80924-97-6.

Supplementary Material Available: NMR and IR spectra of new compounds described in this paper (32 pages). Ordering information is given on any current masthead page.

(29) For example, (a) Alkylation of the C(12) carbaldehyde, cf.: Groenewegen, P.; Kallenberg, H.; van der Gen, A. *Tetrahedron Lett.* **1978**, 491 and references therein. Dietl, H.; Brannock, K. C. *Ibid.* **1973**, 1273. (b) Alkylation of C(12) carbaldimine and metalloenamine equivalents, cf.: House, H. O.; Liang, W. C.; Weeks, P. D. *J. Org. Chem.* **1974**, *39*, 3102. Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178. Martin, S. F.; Phillips, G. W.; Puckette, T. A.; Colapret, J. A. *Ibid.* **1980**, *102*, 5866 and references therein. (c) Quaternization via 2,3-sigmatropic rearrangement of the vinyl sulfonium ylides was unsuccessful, resulting in E2′ elimination of the C(11) alkoxy group, cf.: Evans, D. A.; Sims, C. L.; Andrews, G. C. *J. Am. Chem. Soc.* **1977**, *99*, 5453 and references therein.

(30) See for example: Felkin, H. et al. *J. Am. Chem. Soc.* **1978**, *100*, 6445. Nagata, W.; Mitsuru, Y.; Okumura, T. *Tetrahedron Lett.* **1966**, 847. Cantacuzene, J.; Normant, J. *Ibid.* **1970**, 2947. Namy, J. L.; Boireau, G.; Abenhaim, D. *Bull. Soc. Chim. Fr.* **1971**, 3191 and references therein.

(31) Lau, K. S. Y.; Schlosser, M. J. *J. Org. Chem.* **1978**, *43*, 1595. Ketone **20** was found to be practically unreactive with $(MeO)_2PO$–$CH^-COOMe\ Li^+$ and TMS–$CH^-COOEt\ Li^+$ even under forcing conditions: Shimoji, K.; Taguchi, H.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 1620.

(32) Tanigawa, Y.; Ohta, H.; Sonoda, A.; Murahashi, S. *J. Am. Chem. Soc.* **1978**, *100*, 4610. Approximately 20% of **22** was recovered in addition to ~20% of the α-alkylation product. Assuming the boat-chair conformation for the eight-membered ring[6] (as drawn), γ alkylation was anticipated from an examination of models to occur from the less hindered pseudoequatorial face of the olefin.

(33) Anschütz, R.; Bertram, W. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 466. Brewster, J. H.; Ciotti, C. J. *J. Am. Chem. Soc.* **1955**, *77*, 6214.

(34) Cf. Riedl, K. *J. Antibiot.* **1976**, *29*, 132. Egger, H.; Reinshagen, H. *Ibid.* 915.

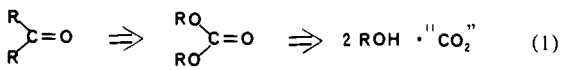
Oxidation of Ketals to Orthocarbonates: A Double Baeyer–Villiger Reaction

William F. Bailey* and Mei-Jue Shih

Department of Chemistry, University of Connecticut
Storrs, Connecticut 06268

Received December 28, 1981

In contrast to the classical Baeyer–Villiger oxidation[1] of ketones to esters, no simple methodology exists for the double oxidation of ketones to carbonates. Herein we report that the formal equivalent of a "double" Baeyer–Villiger reaction is easily accomplished under mild conditions by oxidation of diethyl ketals with peroxycarboxylic acid. This facile double oxidation of ketals to orthocarbonates provides an efficient method for the removal of a carbonyl function from a ketone (see eq 1).



(1)

The oxidation of the symmetrical ketal 3,3-diethoxypentane[2] (**1**) is illustrative of the general reaction.[3] Addition of **1** to a well-stirred suspension of excess (3–4 molar equiv) *m*-chloroperoxybenzoic acid (MCPBA) in dry CH_2Cl_2 (200–250 mL for a 50-mmol scale oxidation) results in an exothermic reaction in which virtually all of the ketal is consumed. The oxidation may become very vigorous following an induction period of 10–30 min (vide infra) and it is often necessary to use an ice-water bath to moderate the exotherm and maintain the reaction temperature between 15–30 °C. After complete oxidation,[4] the entire reaction mixture was poured into a large excess of rapidly stirred, ice-cold 5% aqueous NaOH (ca. 1 L for a 50-mmol scale oxidation). The organic layer was separated, washed successively with 15% aqueous Na_2SO_3 and brine, dried (K_2CO_3), and concentrated. The oxidation of **1** afforded a mixture of products consisting chiefly of diethyl carbonate (**3**), tetraethyl orthocarbonate (**2**), and ethyl *m*-chlorobenzoate along with a small amount of ethyl propionate and 3-pentanone. The carbonate and orthocarbonate may be isolated in a combined yield of 70% (Table I). The low yield of **2** is not unexpected since ortho esters are known to esterify carboxylic acids, producing carbonates and alcohol:[5] $R'CO_2H + (RO)_4C \rightarrow R'CO_2R + (RO)_2C{=}O + ROH$.

The destruction of orthocarbonates via reaction with *m*-chlorobenzoic acid generated from MCPBA is unavoidable.[6] Thus, when less symmetric ketals are oxidized, product separation is often difficult since a mixture of all possible carbonates, benzoates, and alcohols is produced. Although carbonates and esters constitute the bulk of the product mixture, moderate yields (25–40%) of pure orthocarbonates[7] not generally available by other routes[8]

(1) For reviews of the Baeyer–Villiger reaction see: (a) Hassall, C. H. *Org. Reactions* (*N.Y*) **1957**, *9*, 73. (b) Smith, P. A. In "Molecular Rearrangements"; de Mayo, P., Ed.; Wiley-Interscience: New York, 11963, Vol. 1, p 577. (c) Lee, J. B.; Uff, B. C. *Q. Rev., Chem. Soc.* **1967**, *21*, 429. (d) Plesnicar, B. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; part C, p 254.

(2) Carswell, H. E.; Adkins, H. *J. Am. Chem. Soc.* **1928**, *50*, 235.

(3) Diethyl ketals were prepared in high yield from equimolar amounts of ketone and triethyl orthoformate dissolved in excess anhydrous ethanol containing a catalytic quantity of anhydrous HCl generated by addition of acetyl chloride to the dry ethanol.

(4) Oxidations were run until virtually no ketal remained as adjudged by GC or TLC. It should be noted that prolonged reaction times may lead to a variety of secondary products derived from further reaction of the acid labile orthocarbonates, alcohols, etc.

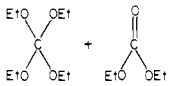
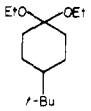
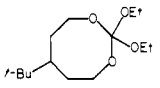
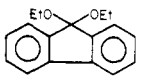
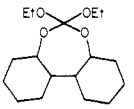
(5) (a) Cohen, H.; Mier, J. D. *Chem. Ind.* (*London*) **1965**, 349. (b) Kantlehner, W.; Funke, B.; Haug, E.; Spek, P.; Kienitz, L.; Maier, T. *Synthesis* **1977**, 73.

(6) Obvious benefit would derive from the use of an oxidant whose reduced form does not react with the orthocarbonate product, and we are actively evaluating other oxidizing agents for use in the ketal → orthocarbonate conversion.

(7) Satisfactory C and H analyses and/or exact mass spectroscopic molecular weights have been obtained for all new compounds (**6**, **9**, **11**, **16**), and their IR, ^1H NMR and ^{13}C NMR spectra are in accord with the assigned structures.

0002-7863/82/1504-1769$01.25/0

Table I. Oxidation of Ketals and Orthoesters to Orthocarbonates

substrate	reaction time, h	product(s)	yield,[a] %
 1	2.5	 2 3	68[b]
 4	2	2 + 3	70[c]
 5	5	 6	25
 7	6	6	31
 8	9	 9	30
 10	6	 11	37
 12	72	unreacted 12 recovered	

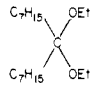
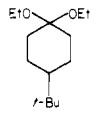
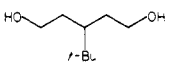
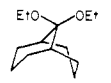
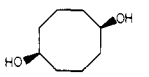
[a] Isolated yield of purified product. [b] 18% 2 and 50% 3. [c] 25% 2 and 45% 3.

may be obtained as shown in Table I if precautions are taken during workup to exclude acidic water. Not surprisingly, ortho esters such as **4** and **7** (Table I) are also rapidly oxidized to orthocarbonates in yields comparable to those for the corresponding ketals.

It should be noted that the 1,3-dioxolane derived from 3-pentanone (**12**) is completely inert to the action of MCPBA (Table I) under conditions that result in the exothermic oxidation of diethyl ketals. This resistance to oxidation appears to be general for 1,3-dioxolane ketals.[9]

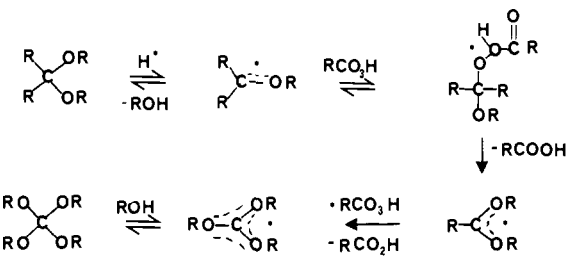
The mixture resulting from oxidation of ketals need not of course be separated if the objective is oxidative removal of the carbonyl group of a ketone via the "double" Baeyer–Villiger reaction. The transformation is best accomplished by lithium aluminum hydride reduction of an etheral solution of the crude carbonate/ester mixture produced upon mild acidic hydrolysis (two phase: CH_2Cl_2 and 0.16 M HCl) of the crude ketal oxidation product. As shown in Table II, the overall sequence ketal → alcohol or diol may be accomplished in good (60–75%) yield.[10]

Table II. Conversion of Diethyl Ketals to Alcohols and Diols

substrate	oxidation time, h	alcohol/diol	yield,[a] %
 13	5		75[b]
 8	13	 15	59
 16	40	 17	65

[a] Isolated yield of purified product. [b] Based on the formation of 2 equiv of 14.

Scheme I



The facile oxidation of ketals is envisioned to proceed via a series of steps entirely analogous to the essential mechanism of the classical Baeyer–Villiger reaction,[1] and the conversion of **16** to *cis*-1,5-cyclooctanediol is consistent with retention of configuration[1] in each of the oxidation steps (see Scheme I).[11] Initiation of the oxidation appears to require a species more acidic than RCO_3H, and for this reason commercial MCPBA containing 10–15% carboxylic acid is a convenient oxidant.[12] Once begun the reaction is autocatalytic since a molecule of RCO_2H is produced in each oxidation step. As noted above, there is often an induction period before the onset of whay may be a *very exothermic reaction* and an ice-water bath should be nearby in case moderation of the exotherm becomes necessary. It should also be noted that in general the "double" oxidation of ketals proceeds much faster and more exothermically then the classical oxidation of the corresponding ketones.

The oxidation of acetals to esters has been well documented[13] but to our knowledge the only prior example of ketal oxidation is an isolated report of the inadvertent conversion of a bicyclic ketal to an ortho ester.[14] The lack of literature precedent for the "double" Baeyer–Villiger oxidation may well be due to the fact that most studies of ketals have focused on cyclic derivatives and, as noted above, the 1,3-dioxolane ketals appear to be resistant to oxidation. We are continuing to explore the scope and synthetic utility of the ketal-to-orthocarbonate oxidation.

Acknowledgment. This research was supported in part by a grant from the Humphrey Chemical Co., North Haven, CT, and

(8) For reviews on the preparations of ortho esters see: (a) De Wolfe, R. H. "Carboxylic Ortho Acid Derivatives"; Academic Press: New York, 1970. (b) De Wolfe, R. H. *Synthesis* **1974**, 153.

(9) The resistance of 1,3-dioxolane ketals to oxidation by MCPBA is presumably related to the unfavorable position of equilibrium between protonated ketal and ring-opened cation in these cyclic ketals. See, for example: McClelland, R. A.; Ahmad, M.; Mandrapilias, G. *J. Am. Chem. Soc.* **1979**, *101*, 970.

(10) Oxidative removal of the carbonyl function from a ketone has traditionally involved a rather large number of operations. The shortest route $R_2CO \rightarrow 2ROH + "CO_2"$ involving classical transformations would seem to be Baeyer–Villiger oxidation of the ketone and hydrolysis of the resulting ester (liberating 1 equiv of ROH) followed by degradation of the acid ($RCO_2H \rightarrow ROH + "CO_2"$) perhaps via carboxy inversion of a diacyl peroxide [Denney, D. B.; Sherman, N. *J. Org. Chem.* **1965**, *30*, 3760].

(11) The stereochemistry of the ketal oxidation is being investigated. A stereoselective "double" Baeyer–Villiger oxidation would be a useful addendum to recent advances in the regio-, diastereo-, and enantioselective alkylations of ketones.

(12) The use of 99+% pure MCPBA [Schwartz, N. N.; Blumbergs, J. H. *J. Org. Chem.* **1964**, *29*, 1976] results in a long induction period prior to the oxidation reaction.

(13) (a) Heywood, D. L.; Phillips, B. *J. Org. Chem.* **1960**, *25*, 1699. (b) Grieco, P. A.; Oguri, T.; Yokoyama, Y. *Tetrahedron Lett.* **1978**, 419. (c) Taillefer, R. J.; Thomas, S. E.; Nadeau, Y.; Fliszar, S.; Henry, H. *Can. J. Chem.* **1980**, *58*, 1138.

(14) Gaoni, Y. *J. Chem. Soc. C* **1968**, 2925, 2934.

in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 36749-09-4; **2**, 78-09-1; **3**, 105-58-8; **4**, 115-80-0; **5**, 23786-93-8; **6**, 80866-27-9; **7**, 53143-91-2; **8**, 1900-58-9; **9**, 80866-28-0; **10**, 80866-29-1; **11**, 80866-30-4; **12**, 4362-57-6; **13**, 80866-31-5; **14**, 111-70-6; **15**, 50635-65-9; **16**, 80866-32-6; **17**, 23418-82-8.

Chemical Reactivity of the New Amino Acid β-Carboxyaspartic Acid (Asa)

M. Robert Christy and Tad H. Koch*

Department of Chemistry, University of Colorado Boulder, Colorado 80303

Received November 20, 1981

We recently reported the laboratory synthesis of the new naturally occurring amino acid β-carboxyaspartic acid (Asa) and its identification in the ribosomal proteins of *E. coli*.[1] Asa is a homologue of γ-carboxyglutamic acid (Gla), which is formed by the vitamin-K-mediated post-translational γ carboxylation of glutamyl residues in blood coagulation proteins.[2] We have reported that Asa from base hydrolysis of the ribosomal proteins of *E. coli* is acid labile with respect to decarboxylation to aspartic acid (Asp).[1] We as well as Hauschka and co-workers have noted similar reactivity for synthetic Asa.[1,3]

Recently, we have observed that Asa is also base labile with respect to elimination of the amine functional group and now report in detail on the decarboxylation and elimination reactions of Asa and of a model system for Asa residues in a protein. The elimination reaction is particularly significant because it limits the detectability of Asa in proteins by alkaline hydrolysis followed by amino acid analysis.

Failure to detect Asa in any protein subjected to acid hydrolysis is due to its quantitative decarboxylation to Asp. The reaction follows clean first-order kinetics in 1 M hydrochloric acid. Plots of $-\ln (A_t - A_\infty)$ vs. time are linear for the entire reaction, where A_t and A_∞ are the absorbances at 207 nm at time t and time ∞. The rate constants as a function of temperature are as follows: 321 K, $(2.06 \pm 0.01) \times 10^{-5}$ s^{-1}; 338 K, $(2.13 \pm 0.02) \times 10^{-4}$ s^{-1}; 343 K, $(3.72 \pm 0.02) \times 10^{-4}$ s^{-1}; 348 K, $(7.56 \pm 0.09) \times 10^{-4}$ s^{-1}. The data give a linear Arrhenius plot with an activation energy of 29.8 ± 0.04 kcal/mol and a preexponential factor of 3.7×10^{15} s^{-1}. Hauschka and co-workers independently determined the free energy of activation to be 26.8 kcal/mol.[3]

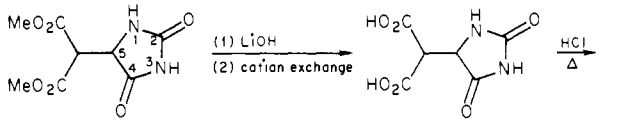
We have investigated the stability of Asa incorporated in a protein with respect to decarboxylation using 5-hydantoinmalonic acid (**1**) as a model system. 5-Hydantoinmalonic acid was synthesized from dimethyl 5-hydantoinmalonate (**2**) by saponification in aqueous tetrahydrofuran solvent (1:2 v/v) with a 2-fold excess of lithium hydroxide at 25 °C for 8 h and was isolated, after cation-exchange chromatography on a column of Hamilton HC-X4.00 resin eluting with 0.10 M hydrochloric acid, as the monohydrate in 73% yield.[4] Dimethyl 5-hydantoinmalonate was prepared in 26% yield by reaction of dimethyl sodiomalonate with 5-chlorohydantoin using a modified version of the procedure reported for the preparation of diethyl 5-hydantoinmalonate.[5]

Table I. Reactivity of β-Carboxyaspartic Acid as a Function of pH

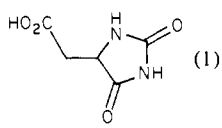
NaOH,[a] equiv	pH	reaction composition, %[b] unreacted Asa	Asp	tricarboxyethylene
1.0	1.8	0	100	0
2.0	4.6	35	50	15
3.0	9.8	74	0	26
3.5	10.0	76	0	24
4.0	12.2	99	0	1

[a] The appropriate quantity of a 2.0 M solution of sodium hydroxide was added to a solution of β-carboxyaspartic acid hydrochloride (~0.1–0.3 mM) in deionized water. [b] Samples were heated to 60 ± 0.2 °C for 64 h in sealed, Teflon-lined vessels and analyzed by ^{1}H NMR spectroscopy in deuterium oxide and hexadeuteriodimethyl sulfoxide solvents.

5-Hydantoinmalonic acid was dissolved in 1.0 M hydrochloric acid and heated in a Teflon-lined, sealed vessel at 70 ± 1 °C for 30 h. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, which indicated that 5-hydantoinmalonic acid cleanly decarboxylated to 5-hydantoinacetic acid (**3**)[6] with first-order



2 1



3 (1)

kinetics. After 30 h the reaction was 82% complete. A plot of −ln (% 5-hydantoinmalonic acid) vs. time gave a first-order rate constant of $(1.41 \pm 0.03) \times 10^{-5}$ s^{-1} and a $\tau_{1/2}$ of 13.7 h. Hence, Asa decarboxylates 25 times faster than 5-hydantoinmalonic acid at 70 °C. Gla is similarly stabilized by peptide bonds.[3]

As shown in Table I, β-carboxyaspartic acid reacts at higher pH by elimination of the amine functional group to give tricarboxyethylene, characterized as its trisodium salt **4** by a singlet at δ 6.28 in its ^{1}H NMR spectrum in deuterium oxide solvent. The identification of **4** was achieved by conversion to 1-hydroxy-1,2,2-tricarboxyethane (**5**)[6] by cation-exchange chromatography and by conversion to the known tricarboxyethane (**6**)[7] with catalytic hydrogenation followed by cation-exchange chromatography. Both **5** and **6** were independently prepared in 95% and 94% yields, respectively, by saponification of tris(carbomethoxyethylene)[8] (**7**) followed by cation-exchange chromatography or followed by catalytic hydrogenation and cation-exchange chromatography. Tricarboxyethane was also prepared in 62% yield by saponification of tris(carbomethoxy)ethane[9] (**8**) followed by cation-exchange chromatography. These reactions are summarized in Scheme I. A control experiment showed that Asa was stable to the condition of catalytic hydrogenation and cation-exchange chromatography.

The stability of Asa under the basic conditions commonly employed for protein hydrolysis was also examined. Heating a

(1) Christy, M. R.; Barkley, R. M.; Koch, T. H.; Van Buskirk, J. J.; Kirsch, W. M. *J. Am. Chem. Soc.* **1981**, *103*, 3935.

(2) Stenflo, J.; Fernlund, P.; Egan, W.; Roepstorff, P. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 2730. Nelsestuen, G. L.; Zythovicz, T. H.; Howard, J. B. *J. Biol. Chem.* **1974**, *249*, 6347. Magnusson, S.; Sottrup-Jensen, L.; Petersen, T. E.; Morris, H. R.; Dell, A. *FEBS Lett.* **1974**, *44*, 189.

(3) Hauschka, P. V.; Henson, E.; Gallop, P. M. *Anal. Biochem.* **1980**, *108*, 57.

(4) 5-Hydantoinmalonic acid hydrate has the following spectroscopic and analytical properties: IR (KBr) 2.75–3.7 (b) and 5.5–6.2 μm (b); ^{1}H NMR (Me_2SO-d_6) δ 3.62 (d, J = 4.5 Hz, 1 H), 4.37 (d, J = 4.5 Hz, 1 H), 7.80 (s, 1 H), 9.30–10.50 (b, 4 H), 10.65 (s, 1 H); ^{13}C NMR (D_2O) δ 52.4 (t, 1:1:1), 57.5, 160.3, 169.8, 170.6, 176.5. Anal. Calcd for $C_6H_8N_2O_7$: C, 32.73; H, 3.66; N, 12.73. Found: C, 32.73; H, 3.67; N, 12.69.

(5) Henson, E. B.; Gallop, P. M.; Hauschka, P. V. *Tetrahedron* **1981**, *37*, 2561.

(6) 5-Hydantoinacetic acid was characterized by comparison of its ^{1}H NMR spectral properties with those of an authentic sample.

(7) 1-Hydroxy-1,2,2-tricarboxyethane polymerized upon attempted further purification and was characterized by an ^{1}H NMR singlet at δ 4.88 and as its trisodium salt by an AB pattern at δ 3.53 and 4.31 (J = 4.5 Hz), both in deuterium oxide solvent.

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

(9) Bischoff, C. A. *Justus Liebigs Ann. Chem.* **1882**, *214*, 38.

0002-7863/82/1504-1771$01.25/0