# Synthesis and Properties of Deltic Acid (Dihydroxycyclopropenone) and the Deltate Ion

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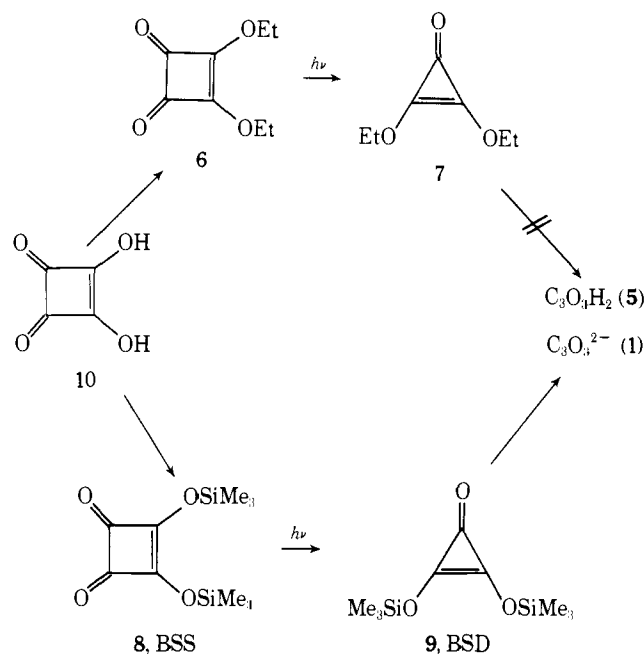
Abstract: Deltic acid (dihydroxycyclopropenone, **5**) has been prepared by reaction of 1-butanol and bis(trimethylsiloxy)cyclopropenone (**9**), which was obtained by photolytic decarbonylation of bis(trimethylsiloxy)cyclobutenedione. Dilithium deltate (**1b**) has also been synthesized from **9** and lithium *tert*-butoxide. The structure of **5** was established by its conversion to dimethoxycyclopropenone, and **1b** was identified by protonation to **5**. The spectral properties of deltic acid and the deltate ion support the structural assignments.

The study of the oxocarbon anions **1–4** began 150 years ago when Gmelin first isolated dipotassium croconate (**3**, potassium salt).[1,2] The rhodizonate ion (**4**) was discovered a few
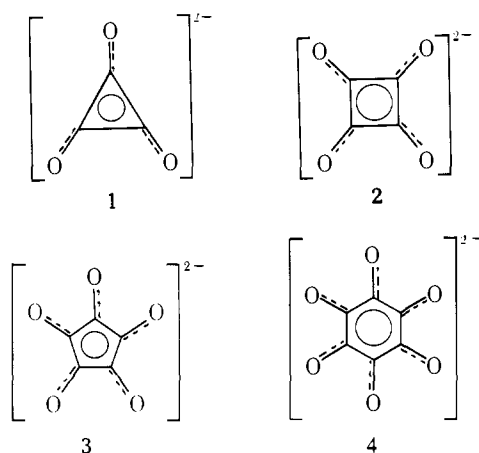
years later,[3] but over a century passed before the squarate ion (**2**) was synthesized.[4] A symmetrical delocalized structure was first proposed for **3** in 1958,[5] and a few years later, salts of **2**, **3**, and **4** were recognized as a new class of aromatic compounds.[6] Early theoretical calculations on the monocyclic anions $C_nO_n^{2-}$ predicted the delocalization energy per π electron to increase from 0.220β for $C_8O_8^{2-}$ to 0.240β for $C_4O_4^{2-}$ (squarate ion). A much larger increase to 0.280β was noted in going from $n = 4$ to $n = 3$, offering hope that extra electronic stabilization in the then unknown deltate ion (**1**, $C_3O_3^{2-}$) might counteract some of the thermodynamic destabilization expected from the increased angle strain and charge density.[7] Although most subsequent MO calculations ignored all but the squarate, croconate, and rhodizonate ions (**2–4**),[8-12] the results of MINDO/2 and CNDO calculations have recently been reported for $C_nO_n^{2-}$, $n = 3-6$.[13] The calculated heats of formation, summarized in Table I, gave a more reasonable prediction about the relative stability of the deltate ion. Although the deltate ion was predicted to have a large negative heat of formation, comparison on a per-atom basis of the calculated ΔH_f's suggested a significantly lower thermodynamic stability relative to squarate (**2**), croconate (**3**), and rhodizonate (**4**).

A number of unsuccessful attempts to synthesize deltic acid (dihydroxycyclopropenone, **5**) or the deltate anion (**1**) have been reported.[14-17] Most recently, the photochemical extrusion of carbon monoxide from diethyl squarate (**6**, diethoxycyclobutenedione) gave diethoxycyclopropenone (**7**), but **7** could not be hydrolyzed to deltic acid.[17] Replacement of the ethyl groups with trimethylsilyl, however, has allowed the synthesis of deltic acid and the deltate ion via bis(trimethylsiloxy)cy-

clobutenedione [**8**, BSS, from *bis*(trimethylsilyl) *s*quarate] and bis(trimethylsiloxy)cyclopropenone [**9**, BSD, from *bis*-(trimethylsilyl) *d*eltate].[18]

Results and Discussion

Synthesis and Properties of Deltic Acid. Since our preliminary communication on the synthesis of deltic acid, which included the preparation of BSS from squaric acid (**10**) and bis(trimethylsilyl)acetamide (BSA),[18] BSS has also been prepared by reaction of silver squarate and trimethylchlorosilane.[19] The structure of BSS, apparent from comparison of its ir spectrum with that of diethyl squarate (**6**),[18] was confirmed by mass spectroscopy, ^{1}H NMR spectroscopy, elemental analysis, and reaction with 1-butanol to give squaric acid (**10**).

Because of the high sensitivity of BSS to atmospheric moisture, the preparation of the corresponding *tert*-butyldimethylsilyl compound **11** was attempted by reaction of lithium *tert*-butyldimethylsilanolate with dichlorocyclobutenedione (**12**), the "acid chloride" of squaric acid.[20,21] The only volatile product obtained was a ring-opened compound in 17% yield identified from spectral data as **13**. The ir spectrum showed an acetylene stretch (2240 cm^{-1}) and an ester carbonyl (1740 cm^{-1}), and the ^{1}H NMR indicated three different *tert*-butyldimethylsilyl groups. The mass spectrum did not show the expected parent at m/e 492, but did have peaks at 477 (loss of methyl) and 435 (loss of butyl), both with strong p + 2 peaks indicative of a chlorine atom.

Table I. Heats of Formation (kcal/mol) of $C_nO_n^{2-}$ from MINDO/2 Calculations[a]

Ion	ΔH_f calcd	ΔH_f calcd/n[b]
$C_3O_3^{2-}$	−78.82	−26.27
$C_4O_4^{2-}$	−161.14	−40.29
$C_5O_5^{2-}$	−206.22	−41.24
$C_6O_6^{2-}$	−225.86	−37.64

[a] From ref 13. [b] n = number of carbons.

Table II. Uv Spectra of Alkyl and Silyl Squarates and Deltates

Compd	λ_{max}, nm (log ϵ) R = alkyl	R = SiMe$_3$
	246 (4.32)[a]	320 sh (3.77), 275 sh (4.27), 258 (4.37), 227 (4.96)
	244 (3.39)[b]	275 sh (2.35), 225 sh (3.26), end absorption to 200

[a] R = methyl, from ref 23. [b] R = ethyl, from ref 17.

12   11

13
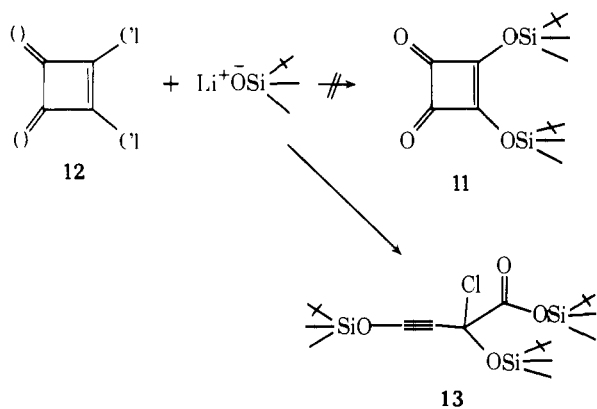
When a solution of BSS in hexane was photolyzed, BSD was obtained in 15-20% yield after purification by Kugelrohr distillation and low-temperature recrystallization.[22] BSD was characterized by ir ($\bar{\nu}$ 1870 and 1655 cm^{-1}, cf. diethoxycyclopropenone (7), 1890 and 1680 cm^{-1} [17]) and ^{1}H NMR spectroscopy.

The uv spectra of BSS and BSD were obtained and are compared with dimethyl squarate (14)[23] and diethoxycyclopropenone (7)[17] in Table II. The extinction coefficients are much larger for the cyclobutenediones than for the cyclopropenones. The near coincidence of the absorption maxima of the alkyl esters, 14 and 7, is probably responsible for the low yield of cyclopropenone 7 if diethyl squarate (6) is completely photolyzed.[17] If photolysis of BSS is carried out through quartz, no BSD is observed, but if a Vycor filter (cutoff at 220 nm) is used, photolysis can be continued until all the cyclobutenedione ir absorption is gone without seriously decreasing the yield of the cyclopropenone, BSD.

When BSD was treated with 2 equiv of 1-butanol at −78 °C, a white solid of empirical formula $C_3O_3H_2$ was formed. The structure was confirmed as dihydroxycyclopropenone (5) by reaction with diazomethane to give dimethoxycyclopropenone (15), identified by comparison of ir, ^{1}H NMR, and mass spectral data with data reported for diethoxycyclopropenone (7).[17] The analogous reaction of squaric acid gave dimethoxycyclobutenedione (14).[23]

Infrared spectroscopy also supports the structural assignment of deltic acid. Squaric acid has a very broad O–H band at ca. 2250 cm^{-1},[24] and deltic acid has a similar broad band

BSD

5   15

10   14
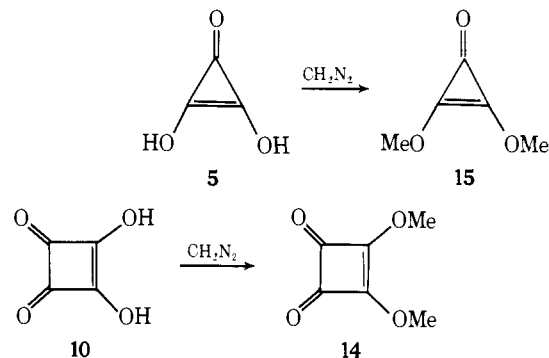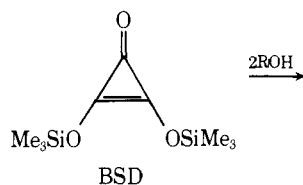
at ca. 2300 cm^{-1}. Diethyl squarate (6) and squaric acid have three cyclobutenedione bands between 1500 and 2000 cm^{-1}, but in the acid, the bands are broader and spread over a greater frequency range.[24] Similarly, dimethoxycyclopropenone (15) and deltic acid have the two expected[25] cyclopropenone bands in the 1500-2000 range which are broader and farther apart in the acid.[26]
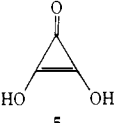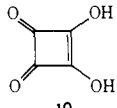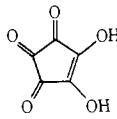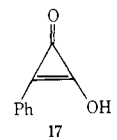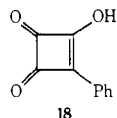
As a solid, deltic acid is stable to atmospheric moisture and oxygen. Deltic acid is insoluble in nonhydroxylic organic solvents, and solution in boiling water immediately gives decomposition to unidentified carboxylic acids. When dissolved in ethanol-water at room temperature, decomposition can be detected after several hours but is incomplete even after several days. The stability in aqueous solution is sufficient to allow pK determinations, and the preliminary results of Schwartz and Gelb indicate a pK_1 of 2.57 and pK_2 of 6.03.[27] By comparison to squaric (10)[28] and croconic acid (16),[29] deltic acid is unexpectedly weak, but the relative acidities of deltic and squaric acids are consistent with the previously reported pK's of phenylhydroxycyclopropenone (17) and phenylhydroxy-cyclobutenedione (18, see Table III).[30]

The thermal stability of solid deltic acid is variable. A sample has been heated gradually to 150 °C without change in the ir spectrum, and slow heating above 150 °C sometimes results in gradual decomposition. Explosive decomposition has also occurred, more frequently on rapid heating, at temperatures as low as 140 °C. Dichlorocyclopropenone is explosively unstable at much lower temperature,[15] and cyclopropenone polymerizes at room temperature.[31]

Synthesis and Properties of the Deltate Ion. When deltic acid was neutralized with 2 equiv of potassium hydroxide, impure dipotassium deltate (1a) was obtained. Treatment of BSD, however, with 2 equiv of lithium tert-butoxide at −78 °C gave dilithium deltate (1b) in 67% yield after precipitation from water with acetone.[32] Identification of 1b is based on elemental analysis, isolation of deltic acid on acidification, and spectral data.

We have not yet obtained crystals suitable for x-ray crystallographic determination of the structure of the deltate ion (1), but vibrational and ^{13}C NMR spectra provide strong evidence for a planar triangular structure. Assuming D_{3h} symmetry, the deltate ion should have four infrared-active and six Raman-active fundamentals, while lower symmetry (C_{2v}, C_2, C_1) should give rise to at least 11 infrared and 12 Raman bands.[33] Since the ir spectrum of dilithium deltate is complicated by strong Li-O bands between 300 and 600 cm^{-1}, dipotassium deltate (1a) was prepared by aqueous metathesis of 1b with potassium fluoride. The ir of 1a showed only four

Table III. pK's of Oxocarbon Acids and Phenyl-Substituted Analogues

Compd	pK$_1$	pK$_2$	Ref
 5	2.57	6.03	27
 10	0.54	3.48	28
 16	0.80	2.24	29
 17	2.01		30
 18	-0.22		30
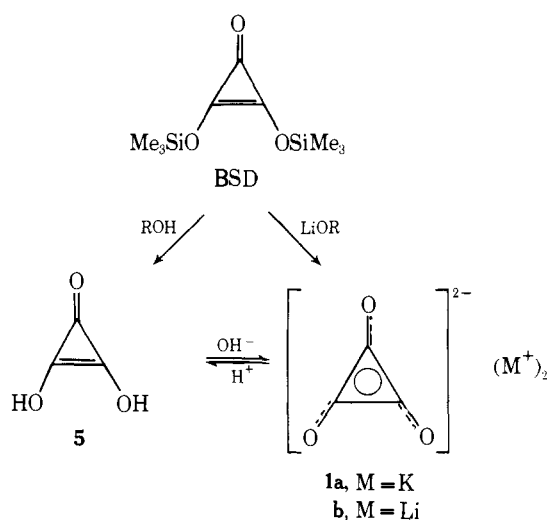
bands which are compared with the spectra of squarate, croconate, and rhodizonate ions in Table IV, and the Raman spectrum showed the expected six fundamentals.[34]

The symmetry of the deltate ion is also shown by the observation of a single line at 140.00 ppm (δ Me$_4$Si) in the ^{13}C NMR spectrum of dilithium deltate in D$_2$O.[35] The 63 ppm upfield shift relative to the squarate ion (δ 203.05)[36] may be partly due to the C(3) ring and partly to the increased C-C and decreased C-O double-bond characters, as predicted by simple resonance theory and by MINDO/2 calculations.[13,37,38]

The uv spectrum of dilithium deltate in water from 210 to 400 nm shows only strong end absorption and a weak shoulder at 240 nm (ϵ 400). The first allowed electronic transition of **1** has been predicted to occur at 223 nm (ϵ 20 000),[13] but if the prediction is adjusted by the amount that the squarate and croconate ions deviate from theory, a more reasonable expectation for **1** is a band at 195-200 nm, consistent with the experimental observation. A weak band (ϵ 170) at 325 nm in the spectrum of the squarate ion has been assigned to an n →

Table IV. Infrared Fundamentals of Oxocarbon Anions, cm^{-1}

	K$_2$C$_3$O$_3$[a]	K$_2$C$_4$O$_4$[b]	K$_2$C$_5$O$_5$[b]	Rb$_2$C$_6$O$_6$[c]
C-O stretch	1445 (s)	1530 (s)	1570 (s)	1490 (s)
C-C stretch	965 (m)	1090 (m)	1100 (vw)	1045 (m)
In-plane C-O bend	325 (w)	350 (w)	374 (w)	395 (w)
Out-of-plane bend	258 (w)	259 (m)	248 (m)	

[a] Assignments for K$_2$C$_3$O$_3$ are tentative pending the results of normal coordinate analysis.[34] [b] M. Ito and R. West, *J. Am. Chem. Soc.*, 85, 2580 (1963). [c] Previously unreported.

π^* transition[39] and a similar assignment can be made for the deltate ion's shoulder at 240 nm.

Experimental Section

General. Squaric acid (**10**) (Aldrich, Columbia Organic) was purified by recrystallization from water. Bis(trimethylsilyl)acetamide (Aldrich) was used as received. All silylated compounds were handled under a dry nitrogen atmosphere. Dichlorocyclobutenedione (**12**) was prepared by the published procedure.[21] *tert*-Butyldimethylsilanol was prepared by reaction of *tert*-butyldimethylchlorosilane (Willow Brook Labs) with potassium hydroxide and purified by distillation.[40] *n*-Butyllithium (Foote Mineral) was standardized for total base. Alcohol-free diazomethane was prepared from Diazald (Aldrich). Acetonitrile (Aldrich) was distilled from calcium hydride and stored over molecular sieve (3A). Hexane (Skelly B) was distilled from potassium and stored over molecular sieve (4A). The photolysis yield was not improved when hexane was treated with fuming sulfuric acid, washed with aqueous bicarbonate and water, and predried (MgSO$_4$) before distilling from potassium. THF (Aldrich) and diethyl ether (Mallinckrodt) were freshly distilled from lithium aluminum hydride.

Spectra were recorded on the following instruments: ir, Perkin Elmer 457; far ir (200-400 cm^{-1}), Digilab FTS-20; Raman, Spex Ramalog; ^{1}H NMR, Varian A-60A; ^{13}C NMR, Varian XL-100, dioxane internal standard (δ 67.405); mass spectra, AEI-MS 902; uv, Cary 14. GLC analysis and separation was carried out on a Barber-Coleman 5340 with a thermal conductivity detector. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Bis(trimethylsiloxy)cyclobutenedione (8, BSS). A mixture of 5.7 g of squaric acid (**10**, 0.050 mol), 21.5 g of bis(trimethylsilyl)acetamide (0.106 mol), and 40 ml of acetonitrile were heated at reflux for 30 min. Acetonitrile and trimethylsilylacetamide (bp 45-60 °C, 0.2 Torr) were removed under vacuum, and the residual material was Kugelrohr distilled (102-106 °C, 0.04 Torr) to yield 10.5 g of BSS (82%): ir (CCl$_4$) 2960 (w), 1820 (m), 1745 (s), 1610 (s), 1400 (s), 1255 (s), 1070 (m), 990 (m), 845 cm^{-1} (br, s); ^{1}H NMR (CCl$_4$) δ 0.44 (s); uv (hexane) λ 320 nm sh (log ϵ 3.77), 275 sh (4.27), 258 (4.37), 227 (4.96); mass spectrum (70 ev) m/e (rel intensity) 260 (1), 259 (1), 258 (5, M$^+$), 245 (2), 244 (3), 243 (7), 204 (4), 203 (7), 202 (17), 149 (5), 148 (9), 147 (25), 146 (4), 101 (7), 77 (7), 75 (8), 74 (10), 73 (100), 45 (13), 44 (3), 43 (6); m/e 258.07433 (calcd for C$_{10}$H$_{18}$Si$_2$O$_4$, 258.07435). Anal. Calcd for C$_{10}$H$_{18}$O$_4$Si$_2$: C, 46.48; H, 7.02; Si, 21.74. Found: C, 46.56; H, 7.14; Si, 22.02.

Reaction of Bis(trimethylsiloxy)cyclobutenedione with 1-Butanol. To an ice-cold solution of 1.20 g (4.65 mmol) of BSS in 10 ml of dry hexane was added 0.85 ml of 1-butanol (9.3 mmol). After 30 min stirring at 0 °C, the white ppt was collected by filtration, dried in vacuo, and identified by its electronic spectrum in 0.01 N aqueous sodium hydroxide as squaric acid. The isolated yield of squaric acid was determined from the literature value of the extinction coefficient[41] to be 92%.

Reaction of Dichlorocyclobutenedione (12) and Lithium *tert*-Butyldimethylsilanolate. A solution of 1.06 g (8.0 mmol) of *tert*-butyldimethylsilanol in 15 ml of THF was cooled to -78 °C, treated with 5.0 ml (8.0 mmol) of 1.60 N *n*-butyllithium, allowed to warm to room temperature, and cooled again to -78 °C. A solution of 0.50 g (3.8 mmol) of **12** in 5 ml of THF was added dropwise, stirred briefly, and allowed to warm to room temperature. Evaporation of solvent and Kugelrohr distillation (110 °C, 0.2-0.3 Torr) yielded 0.32 g (17%) of *tert*-butyldimethylsilyl 2,4-bis(*tert*-butyldimethylsiloxy)-2-chloro-but-3-ynoate (**13**): ir (neat) 2960 (s), 2940 (s), 2900 (m), 2870 (s), 2240 (m), 1740 (s), 1605 (m), 1480 (m), 1470 (m), 1300 (s), 1265

(s), 1180 (s), 1110 (s), 880 (s), 855 (s), 800 cm^{-1} (s); ^{1}H NMR (CCl$_4$) δ 0.90 (s, 9 H), 0.85 (s, 18 H), 0.23 (s, 6 H), 0.13 (s, 6 H), and 0.10 (s, 6 H); mass spectrum m/e (rel intensity) 479 (1), 477 (2, M$^+$ − CH$_3$), 437 (14), 436 (9), 435 (28, M$^+$ − C$_4$H$_9$), 409 (3), 407 (6), 335 (9), 334 (5), 333 (19), 306 (2), 304 (4), 191 (3), 189 (6), 149 (4), 148 (6), 147 (30), 75 (93), 73 (100). GLC analysis (20% QF-1, 15 ft × ¼ in., 165–170 °C) showed one peak at 42 min, and a sample obtained by preparative GLC had an ir identical with the Kugelrohr distillate.

Bis(trimethylsiloxy)cyclopropenone (9, BSD). A solution of 8.8 g (0.034 mol) of BSS in hexane was irradiated for 160 h (to disappearance of the ir bands of BSS) by a 450-watt Hanovia mercury lamp filtered through Vycor. The solution was concentrated and distilled (Kugelrohr apparatus, 25–90 °C, 0.1 Torr) to give a light-yellow viscous liquid which was redistilled, recrystallized from 10-ml portions of hexane at −78 °C until the mother liquor was colorless, and redistilled (Kugelrohr, 71–74 °C, 0.15 Torr) to yield 1.52 g (20%) of low-melting white solid BSD: ir (CCl$_4$) 2960 (m), 1870 (m), 1655 (s), 1325 (s), 1255 (s), 1070 (m), 960 (m), 850 (s), 650 cm^{-1} (m); ^{1}H NMR (CCl$_4$) δ 0.39 (s); uv (hexane) λ sh 275 nm (log ϵ 2.35) 225 sh (3.26).

Dihydroxycyclopropenone (5, Deltic Acid). An ethereal solution of 1.52 g (6.61 mmol) of BSD in 15 ml of ether was cooled to −78 °C and treated with 1.25 ml (13.5 mmol) of 1-butanol. After warming to room temperature, the volatile materials were removed under vacuum to a cold trap, leaving 0.55 g (98%) of solid **5**: ir (KBr) ca. 2300 (s, v br), 1980 (w), 1935 (w), 1605 (s, br), 1450 (s, br), 1390 (s, br), 1020 (m), 960 (m), 900 (w), 775 (w), 750 (w), 410 cm^{-1} (s). Anal. Calcd for C$_3$O$_3$H$_2$: C, 41.87; H, 2.35. Found: C, 41.79; H, 2.43.

GLC analysis (20% SE-30, 15 ft × ¼ in., 110 °C) of the cold trap residue indicated the presence of n-butoxytrimethylsilane in 81% yield identified by its infrared spectrum.[42]

Dimethoxycyclopropenone (15). An alcohol-free ethereal solution of diazomethane (from 11.7 mmol of Diazald) was dried (KOH) and decanted onto 0.178 g (2.06 mmol) of deltic acid and stirred at 0 °C for 45 min. The excess diazomethane was removed by a nitrogen stream, ether was removed under reduced pressure, and the residue was Kugelrohr distilled under high vacuum to yield 0.179 g (77%) of **15**: ir (CCl$_4$) 2950 (w), 2850 (w), 1890 (m), 1680 (s), 1455 (m), 1305 (s), 1030 cm^{-1} (m); ^{1}H NMR (CCl$_4$) δ 4.10 (s); mass spectrum m/e (rel intensity) 114 (24, M$^+$), 86 (100), 68 (38), 56 (59), 45 (30); m/e 114.01368 (calcd for C$_5$H$_6$O$_3$: 114.01368).

Dilithium Deltate (1b). A solution of 1.56 g (6.8 mmol) of BSD in 10 ml of THF was added slowly to 14 mmol of lithium $tert$-butoxide in 20 ml of THF at −78 °C. After stirring at −78 °C for 15 min, the clear solution was warmed to room temperature and evaporated to yield 0.99 g of yellow solid. Solution in 10 ml of water and addition of 30 ml of acetone gave a white ppt which was filtered, washed with acetone, and dried under vacuum to yield 0.44 g (67%) of anhydrous dilithium deltate (**1b**): ir (KBr) 1450–1480 (s, br), 990 (s), 970 (s), 795 (w), 530 (s), 470 (s), 420 cm^{-1} (s); uv (water) λ sh 240 nm (log ϵ 2.61); ^{13}C NMR (D$_2$O) δ 140.00. Anal. Calcd for Li$_2$C$_3$O$_3$: C, 37.14; Li, 14.17. Found: C, 36.88; H, none or trace; Li, 13.90.

Deltic Acid (5) from Dilithium Deltate (1b). A solution of 0.060 g (0.61 mmol) of **1b** in 0.8 ml of water at 0 °C was treated with 1.5 ml of cold 12 N hydrochloric acid, filtered immediately, and dried at high vacuum to give 0.0295 g (56%) of deltic acid (**5**), identified by comparison of its ir spectrum with an analytically pure sample.

Spectral Sample of Dipotassium Deltate (1a). A solution of 0.0182 g (0.186 mmol) of **1b** in 0.20 ml of water was treated with 0.0358 g (0.380 mmol) of potassium fluoride dihydrate. After centrifuging, the clear supernatant was decanted from the lithium fluoride ppt and evaporated to yield **1a** contaminated with a small amount of lithium fluoride: ir (KBr pellet) 1445 (s), 965 (m); 325 cm^{-1} (w); far ir (CsI pellet) 325 (w), 258 cm^{-1} (w); Raman (neat) 1818 (w), 1432 (w), 1383 (w), 1378 (w), 966 (s), 786 (s), 689 (m), 321 (s), 178 (s), 125 (sh, s), 92 cm^{-1} (s).

Dirubidium Rhodizonate was prepred by crystallization from oxygen-free water of sodium rhodizonate and rubidium chloride:[43] ir (Nujol–Fluorolube composite) 1490 (s), 1045 (m), 395 cm^{-1} (w).

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