Anal. Calcd for $C_6H_{10}N_2O_3$: C, 45.56; H, 6.37. Found: C, 46.03; H, 6.03. Acceptable microanalysis for N could not be obtained.

B. Synthesis by Standard Methods. To a stirred solution of 2-methoxyethylamine (60.0 g, 0.80 mol) in benzene (200 mL) at 25 °C was added (over 0.5 h) ethyl 2-bromopropanoate (69.7 g, 0.39 mol) and the mixture stirred for 12 h. The mixture was then diluted with ethyl acetate (200 mL), washed with 140 mL of 10% NaOH, and distilled to produce ethyl 2-[(2-methoxyethyl)amino]propanoate (52.5 g, 78%): bp 90 °C (18 torr); ^{1}H NMR ($CDCl_3$) δ 1.27 (t, CH_3CH_2, J = 7.1 Hz), 1.30 (d, CH_3CH, J = 6.9 Hz), 1.88 (s, NH), 2.74 (m, CH_2N), 3.35 (s, CH_3O) 3.40 (m, $CHCH_3$), 3.48 (m, CH_2O), 4.19 (q, CH_2CH_3); mass spectrum (EI), m/e 176 [10, $(M + 1)^+$], 130 (47), 102 (100), 70 (45), 56 (72).

The ester (30 g, 0.17 mol) was hydrolyzed with boiling 15% NaOH (50 mL) for 0.5 h. The mixture was acidified (pH 5) with 36% HCl (17 mL) and evaporated in vacuo. The residue was extracted with cold chloroform–1-butanol (4:1, 3 × 70 mL) to remove inorganic solids. The organic extract was evaporated in vacuo and the residue dissolved in a pH 5.5 phosphate buffer (30 mL). This solution was again evaporated in vacuo. Extraction of the residue with chloroform–1-butanol (4:1, 2 × 50 mL) provided 2-[(2-methoxyethyl)amino]propanoic acid (20.2 g, 81%): mp 223–225 °C dec; ^{1}H NMR (D_2O) δ 1.21 (d, CH_3CH, J = 7.2 Hz), 2.95 (m, CH_2N), 3.11 (s, CH_3O), 3.37 (m, $CHCH_3$), 3.46 (m, CH_2O); mass spectrum (EI), m/e 147 (1, M^+), 129 [1, $(M - CO_2)^+$], 102 (100), 56 (70). Anal. Calcd for $C_6H_{13}NO_3$: C, 48.97; H, 8.90; N, 9.52. Found: C, 48.86; H, 8.70; N, 9.50.

The unrecrystallized amino acid hydrochloride served well in these next steps. The salt (27.5 g, 0.15 mol) was dissolved in water (50 mL) containing 36% HCl (1 mL). An aqueous solution of sodium nitrite (13.8 g, 0.2 mol in 10 mL) was added dropwise over 0.5 h. The temperature of the reaction mixture was kept between 0 and −5 °C. After an additional 0.5 h of stirring, the mixture was extracted with ethyl acetate (50 mL), dried (Na_2SO_4), and evaporated in vacuo.

The crude *N*-nitroso acid was immediately dissolved in freshly distilled acetic anhydride (150 mL) and stored in the dark at 25 °C for 4 days. Solvents were removed in vacuo at 45 °C (or less) and the residue dissolved in dichloromethane (100 mL). The organic phase was washed with 10% $NaHCO_3$ (until no further CO_2 evolution was observed) and dried (Na_2CO_3). Vacuum evaporation furnished **7** (9.5 g), which was identical in all respects with the product from preparation A. This product was used in the next step.

1-(2-Methoxyethyl)-5-methyl-3,4-pyrazoledicarboxylic Acid (8b). A solution of **7** (10 g, 0.063 mol) and methyl acetylenedicarboxylate (10 g, 0.07 mol) in benzene (100 mL) was refluxed for 18 h. Fractional distillation yielded **8a** (13.1 g, 81%): bp 216–218 °C (30 torr); ^{1}H NMR ($CDCl_3$) δ 2.51 (s, CH_3C), 3.28 (s, CH_3OCH_2), 3.78 (m, CH_2O), 3.84, 3.92 (s, ester CH_3's), 4.27 (m, CH_2N); mass spectrum (EI), m/e 256 (5, M^+), 226 (20), 225 (52), 194 (100), 167 (55), 166 (56), 59 (27), 58 (67).

This ester (13.1 g, 0.051 mol) was hydrolyzed in boiling methanol (10 mL) containing 7 N NaOH (35 mL) for 4 h. After **8a** was absent (TLC; chloroform–methanol, 9:1, R_f 0.56), the solution was concentrated in vacuo and extracted with dichloromethane (2 × 50 mL). The aqueous layer was acidified with 36% HCl (30 mL) and evaporated in vacuo. The residue was triturated several times with methanol–chloroform (1:1, 200 mL). The organic extract yielded **8b**, which was recrystallized from water (8.6 g, 74%): mp 163.5–164.5 °C; TLC (ethyl acetate–ethanol–acetic acid, 85:15:5), R_f 0.24; ^{1}H NMR ($CDCl_3$) δ 2.65 (s, CH_3C), 3.29 (s, CH_3O), 3.77 (m, CH_2O), 4.36 (m, CH_2N), 7.58 (br, OH); mass spectrum (EI), m/e 228 (1, M^+), 180 (47), 58 (100), 45 (86). Anal. Calcd for $C_9H_{12}N_2O_5$: C, 47.37; H, 5.30; N, 12.27. Found: C, 47.44; H, 5.24; N, 12.23.

1-[2-[(4-Methylphenyl)thio]ethyl]-5-methyl-3,4-pyrazoledicarboxylic Acid (8d). A solution of **1a** (2.8 g, 0.011 mol) and methyl acetylenedicarboxylate (1.7 g, 0.012 mol) in benzene (35 mL) was refluxed for 18 h. Solvents were evaporated in vacuo to yield an oily residue. Attempts to distill the ester (0.15 torr) caused partial decomposition although GC/MS analysis showed that **8c** was the major product. Mass spectrum (EI), m/e 348 (5, M^+), 151 (100), 135 (60), 123 (25). The residual oil was hydrolyzed by refluxing for 1 h in a mixture of methanol (20 mL) and 0.5 N NaOH (60 mL) and then the mixture was allowed to stand overnight (25 °C). Partial evaporation in vacuo and addition of 36% HCl (3 mL) precipitated **8d**. The product was filtered, washed with benzene (2 × 100 mL), and recrystallized from water (2.9 g, 81%): mp 198.5–199.5 °C; ^{1}H NMR ($CDCl_3$, 20% CD_3OD) δ 2.31 (s, CH_3Ar), 2.54 (s, CH_3C), 3.39 (t, CH_2S, J = 6.5 Hz), 4.38 (t, CH_2N), 6.98–7.32 (m, Ar H); mass spectrum (EI), m/e 320 (2, M^+), 151 (100), 135 (60), 44 (100). Anal. Calcd for $C_{15}H_{16}N_2SO_4$: C, 56.24; H, 5.03; N, 8.74. Found: C, 56.50; H, 5.08; N, 8.82.

Acknowledgment. We thank Dr. Kenneth F. King and his Associates of the G.D. Searle Co., Skokie, IL, for the interest and support they have shown for this project.

Registry No. 1b, 53492-58-3; **7**, 82581-94-0; **8a**, 82581-95-1; **8b**, 82581-96-2; **8d**, 82581-97-3.

1,3-Butadiene-1,1,4-tricarboxylic Acids

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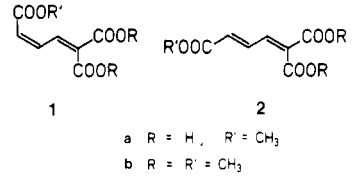
(1*E*,3*Z*)-1,3-Butadiene-1,2,4-tricarboxylic (β-carboxy-*cis*,*cis*-muconic) acid is of considerable biochemical importance as an intermediate in catabolism of aromatic compounds by bacteria and fungi, being formed by intradiol oxidative ring cleavage of 3,4-dihydroxybenzoate.[2] A characteristic and early-recognized[3] property of this triacid is its very rapid stereomutation to the 3*E* isomer under acidic conditions.[4] In this paper we describe the isomeric 1,3-butadiene-1,1,4-tricarboxylic (α-carboxymuconic) acids. The characteristic feature of the *Z* isomer, a potential product of enzymatic degradation of 2,3-dihydroxybenzoate, is its rapid, reversible lactonization in neutral or acidic solutions.

The oxidation of 2-hydroxy-3-methoxybenzaldehyde with chlorous acid to the monoester **1a** of (*Z*)-1,3-butadiene-1,1,4-tricarboxylic acid has been described elsewhere.[5] Diazomethane methylation of **1a** afforded triester **1b**. The corresponding derivatives **2a** and **2b** of (*E*)-1,3-butadiene-1,1,4-tricarboxylic acid were obtained by light- or heat-induced isomerization of **1a** and **1b**, respectively, in the presence of catalytic amounts of iodine. The change of stereochemistry caused characteristic changes in ^{1}H NMR and UV spectra (Tables I and II), reflecting planar conformations[6] of both series.



Hydrolysis of **2a** with alkali, followed by acidification, gave triacid **2c**. However, similar treatment of **1a** yielded the lactone **3** rather than the triacid **1c**. The trianion of **1c**, formed initially by saponification of **1a**, was stable in the presence of excess base and could be characterized by ^{1}H NMR and UV spectroscopy (Tables I and II), but

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(2) See, e.g.: Dagley, S. *Adv. Microb. Physiol.* **1971**, *6*, 1. Stanier, R. Y.; Ornston, L. N. *Ibid.* **1973**, *9*, 89.
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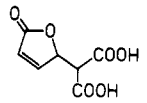
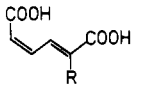
acidification of its solutions with hydrochloric acid to pH 1–2 caused complete and apparently instant (^{1}H NMR, UV) cyclization to **3**.[7] In neutral or slightly acidic solutions



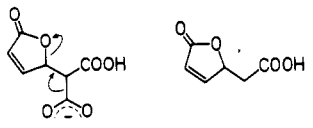
3

the cyclic and open-chain forms coexisted in a pH-dependent equilibrium. Thus, at pH 7.0, 6.0, and 5.0 (0.2 M citrate–phosphate buffers) the proportion of open-chain species (anions of **1c**) in equilibrium was respectively about 82%, 35%, and 5.5%, corresponding to equilibrium constants of 4.5, 0.54, and 0.06. The apparent first-order rates of approach to equilibrium from either side (lactone or open chain) decreased with increasing pH and corresponded to half-lives of 20 or 40 s at 25 °C and pH 5.2 or 6.0, respectively.

When a slightly acidic (pH 3) solution of **3** was heated for several minutes at 100 °C, (2*E*,4*Z*)-2,4-hexadienedioic acid (**4a**) was formed. At this pH the lactone was present



4a R = H
b R = D



5 6

to a large extent as the monoanion (cf. pK_1 of propanedioic acid of 2.8), which can undergo decarboxylative elimination as depicted in **5**. In more acidic or more basic solutions the formation of **4a** was in fact slower. In deuterium oxide the specifically deuterated product **4b** was obtained as the result of rapid exchange of the α-hydrogen in **3**. By contrast, pyrolytic decarboxylation of **3** yielded **6**.

The remarkable facility of the lactonization of **1c** under neutral or weakly acidic conditions is evidently due to conjugation of the C1–C2 double bond with the two geminal carboxy groups. Thus the sequence of nucleophilic attack of the 4-carboxy group at C2 followed by protonation of C1 is faster than nucleophilic attack of the (*Z*)-1-carboxy group at C3, which would lead, upon its reversal before protonation on carbon, to stereomutation of the C3–C4 double bond,[4,6] giving **2c**. Stereomutation of **1a** and **1c** may occur by this mechanism but is slow,[8] perhaps resembling in rate the stereomutation of (2*Z*,4*Z*)-2,4-hexadienedioic acid.[9,10] The stereomutation of (1*E*,3*Z*)-1,3-butadiene-1,2,4-tricarboxylic acid,[4] on the other hand, is sterically accelerated like that of other 3-substituted (2*Z*,4*Z*)-2,4-hexadienedioic acids that cannot attain planar conformations.[6]

The formation of **1c** has been claimed to occur on oxidation of 2,3-dihydroxybenzoate by crude enzyme preparations from the flowering plant *Tecoma stans* (L.) HBK. (Bignoniaceae).[11] However, the properties of the product of the enzymatic reaction, which in our opinion was not satisfactorily characterized, do not match those of **1c** disclosed in the present work. Additional evidence should thus be provided before the formation of **1c** and the existence in *T. stans* of the enzyme 2,3-dihydroxybenzoate 2,3-dioxygenase (EC 1.13.11.28) can be accepted. We believe that our work, providing an account of the basic chemistry of **1c**, may be helpful in identification of this compound in biological systems.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 60 MHz with a Bruker HX60 on Varian T60A spectrometer. Simulation of the spectra was performed on a Varian 620/i computer by using the SIMEQ program.[12] IR and UV spectra were run on Perkin-Elmer Model 457 and Unicam SP1800 instruments, respectively. Melting points were determined in capillaries and are corrected; for compounds melting with decomposition the bath was preheated to 140–150 °C. Combustion analyses were conducted in the microanalytical department of this Laboratory.

Trimethyl (*Z*)-1,3-Butadiene-1,1,4-tricarboxylate (1b). The monomethyl ester **1a**[5] (0.5 g) was methylated with diazomethane in ether to give, after recrystallization from ether–petroleum ether, 0.45 g (79%) of **1b**: mp 49.5–50 °C; IR (KBr) 1740–1720 (s), 1635 (m), 1590 (m) cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30. Found: C, 52.53; H, 5.23.

(*E*)-4-(Methoxycarbonyl)-1,3-butadiene-1,1-dicarboxylic Acid (2a). The monoester **1a**[5] (1.2 g) in acetonitrile (100 mL) containing I_2 (0.1 g) was irradiated (Pyrex-filtered radiation from a mercury source) during 2 h. Evaporation and crystallization from ether–petroleum ether gave 1 g (83%) of **2a**: mp 175 °C dec; IR (KBr) 3250–2500 (s), 1740–1700 (s), 1610 (s) cm^{-1}.

Anal. Calcd for $C_8H_8O_6$: C, 48.01; H, 4.03. Found: C, 47.95; H, 4.20.

Trimethyl (*E*)-1,3-Butadiene-1,1,4-tricarboxylate (2b). The triester **1b** (0.5 g) was refluxed in 150 mL of toluene with 10 mg of I_2 during 1 h. Evaporation and crystallization from ether–petroleum ether gave 0.4 g (80%) of **2b**: mp 67–68 °C; IR (KBr) 1730–1720 (s), 1600 (m) cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30. Found: C, 52.55; H, 5.40.

(*E*)-1,3-Butadiene-1,1,4-tricarboxylic Acid (2c). The monoester **2a** (0.5 g) was hydrolyzed in 10 mL of 5% NaOH during 3 h at room temperature. The solution was saturated with NaCl, acidified with 2 M HCl, and extracted with six 50-mL portions of ethyl acetate. The extracts were dried ($MgSO_4$), concentrated, and allowed to crystallize slowly at 0 °C to give 0.35 g (75%) of **2c**: mp 180 °C dec; IR (KBr) 3300–2400 (s), 1720–1680 (s), 1630 (s), 1595 (s) cm^{-1}.

Anal. Calcd for $C_7H_6O_6$: C, 45.17; H, 3.25. Found: C, 45.28; H, 3.39.

2-(2,5-Dihydro-5-oxo-2-furyl)propanedioic Acid (3). The monoester **1a**[5] (0.3 g) was hydrolyzed as described for **2a** to give 0.23 g (83%) of **3**; mp 160 °C dec (after recrystallization from

(7) Although the tetraethyl ester of 1,3-butadiene-1,1,4,4-tetracarboxylic acid, a counterpart of **1c**, is known, the tetraanion of this acid as well as lactonic products expected to be formed from the anion on acidification have yet to be characterized: Benary, E.; Schinkopf, R. *Ber. Dtsch. Chem. Ges.* **1923**, *56*, 354. Baganz, H.; Müller, R. *Chem. Ber.* **1961**, *94*, 2132.

(8) When aged (5–10 h) solutions containing the mixture of **1c** and **3** (pH 4–7) were acidified to lactonize all **1c**, a weak absorption with a maximum at 270 nm, probably due to **2c**, remained. Such a slow $Z \rightarrow E$ isomerization was also observed by ^{1}H NMR for **1a** when allowed to stand during prolonged periods in deuterium oxide or acetone-d_6.[10]

(9) Elvidge, J. A.; Linstead, R. P.; Sims, P.; Orkin, B. A. *J. Chem. Soc.* **1950**, 2235.

(10) Note that the monomethyl ester of (2*Z*,4*Z*)-2,4-hexadienedioic acid apparently stereomutates more difficultly than the diacid: Elvidge, J. A.; Linstead, R. P.; Sims, P. *J. Chem. Soc.* **1953**, 1793.

(11) Sharma, H. K.; Jamaluddin, M.; Vaidyanathan, C. S. *FEBS Lett.* **1972**, *28*, 41. Sharma, H. K.; Vaidyanathan, C. S. *Eur. J. Biochem.* **1975**, *56*, 163; *Phytochemistry* **1975**, *14*, 2135. Cf.: Vaidyanathan, C. S. *J. Sci. Ind. Res.* **1976**, *35*, 730. Kishore, G.; Sugumaran, M.; Vaidyanathan, C. S. *Ibid.* **1977**, *36*, 332. Sugumaran, M.; Kishore, G.; Subramanian, V.; Mohan, V. P.; Vaidyanathan, C. S. *J. Indian Inst. Sci. Sect. C* **1977**, *59*, 1. Sugumaran, M.; Vaidyanathan, C. S. *Ibid.* **1978**, *60*, 57. See also: Mohan, V. P.; Kishore, G.; Sugumaran, M.; Vaidyanathan, C. S. *Plant Sci. Lett.* **1979**, *16*, 267.

(12) Written by C. W. F. Kort, Laboratory of Organic Chemistry, University of Amsterdam. Computational facilities provided by Dr. K. Schaumburg, Chemical Laboratory V, University of Copenhagen, are gratefully acknowledged.

Table I. ^{1}H NMR Spectral Data of 1,3-Butadiene-1,1,4-tricarboxylic Acids and Esters[a]

compd[b]	chemical shift, δ					coupling constants, Hz		
	$COOCH_3$	COOH	H2	H3	H4	$^3J_{2,3}$	$^3J_{3,4}$	$^4J_{2,4}$
1a	3.78	11.4	8.68	7.32	6.26	11.5	11.5	−1.0
1b[c]	3.78, 3.82, 3.86		8.53	6.97	6.08	11.5	11.5	−1.0
1c[d]			7.35	6.40	6.05	11.5	11.5	e
2a	3.77	11.7	7.65	7.90	6.59	11.8	15.6	−0.65
2b	3.79, 3.82, 3.90		7.49	7.55	6.55	12.1	15.5	−0.65
2c[f]		12.1	7.38	7.42	6.48	11.8	15.7	−0.8

[a] Recorded at 60 MHz. The spectra of 2a-c were solved by ABX treatment and the solutions confirmed by computer simulation of the patterns. [b] Ca. 5%, in $(CD_3)_2CO$ unless otherwise stated. [c] In $CDCl_3$. [d] In D_2O/NaOD, generated in situ from 1a. [e] No coupling observed. [f] In $(CD_3)_2SO$.

Table II. Electronic Spectra of 1,3-Butadiene-1,1,4-tricarboxylic Acids and Esters

compd	solvent	λ_{max}, nm	ϵ_{max}, L mol^{-1} cm^{-1}
1a	0.1 M HCl	269	20 000
1a	0.1 M phosphate buffer, pH 7	280	17 500
1b	CH_3OH	265	20 000
1c[a]	0.1 M NaOH	271	17 100
2a	0.1 M HCl	271	25 000
2b	CH_3OH	266	25 000
2c	0.1 M HCl	270	25 000
2c	0.1 M NaOH	276	21 700

[a] Generated in situ from 1a.

ether-petroleum ether); IR (KBr) 3300-2500 (s), 1755 (s), 1730-1700 (s), 1600 (m) cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 3.85 (Hα), 5.64 (H2), 6.28 (H4), 7.89 (H3), 11.4 (COOH) ($^3J_{2,\alpha}$ = 8 Hz, $^3J_{2,3}$ = 1.6 Hz, $^3J_{3,4}$ = 6 Hz, $^4J_{2,4}$ = 2.1 Hz); ^{1}H NMR (D_2O) δ 5.80 (H2), 6.37 (H4), 7.95 (H3), Hα exchanged for deuterium ($^3J_{2,3}$ = 1.5 Hz, $^3J_{3,4}$ = 6 Hz, $^4J_{2,4}$ = 2 Hz).[13]

Anal. Calcd for $C_7H_6O_6$: C, 45.17; H, 3.25. Found: C, 44.96; H, 3.23.

Equilibrium between 1c and 3. Solutions of the trisodium salt of 1c, prepared by hydrolysis of 1a in 0.1 M NaOH and dilution with water, were added to 0.2 M citrate-phosphate buffers to give solutions with λ_{max} 271 nm (ϵ_{max} 14000) (pH 7.0), 272 (6000) (pH 6.0), and 274 (920) (pH 5.0). Identical ultraviolet spectra were obtained by adding a solution of 3 in 0.01 M HCl to the same buffers. Approximate equilibrium constants (see text) were calculated by assuming the absorptivity of anions of 1c present in the equilibrium mixtures to be identical with that of the trianion in 0.1 M NaOH (Table II).

Acidification of the above equilibrium mixtures with 3 M HCl resulted in formation of 3 and thus in complete loss of ultraviolet absorption.[8] The lactonization could also be observed directly by ^{1}H NMR spectroscopy in D_2O solutions. Rates of approach to equilibrium at pH 5.2 and 6.0 were measured by following changes of ultraviolet absorption at 272 nm after addition of solutions of the trisodium salt of 1c in 0.01 M NaOH or of 3 in 0.01 M HCl to 0.2 M citrate-phosphate buffers at 25 °C.

Decarboxylation of 3. The lactone 3 (0.2 g) was dissolved in 5 mL of water, the pH was adjusted to ca. 3 with 0.1 M NaOH, and the solution was boiled several minutes, acidified with 2 M HCl, saturated with NaCl, and extracted with several 20-mL portions of ethyl acetate to give 0.1 g (65%) of 4a; mp 188-191 °C (after recrystallization from ether) (lit.[9] mp 190-191 °C); UV (0.1 M HCl) λ_{max} 262 nm (lit.[14] 263 nm in 1 M acid); IR spectrum as reported;[15] ^{1}H NMR [$(CD_3)_2CO$] δ 6.10 (H5), 6.29 (H2), 6.90 (H4), 8.52 (H3), 11.5 (COOH) ($^3J_{2,3}$ = 15.5 Hz, $^3J_{3,4}$ = 11.5 Hz, $^3J_{4,5}$ = 11.5 Hz).[16] When a similar decarboxylation was performed in D_2O, the ^{1}H NMR spectrum of the solution corresponded to (2*E*,4*Z*)-2,4-hexadiene-2-*d*-dioic acid (4b): δ 6.10 (H5), 6.67 (H4), 7.98 (H3) ($^3J_{3,4}$ = 11.5 Hz, $^3J_{4,5}$ = 11.5 Hz; the signal of H3 broadened owing to coupling with deuterium).

Heating solutions of 3 at pH 5-6, where some ionized 1c present at equilibrium gave rise to ultraviolet absorption at 272-274 nm, caused the maximum to shift to 265-267 nm with an increase of intensity as a result of formation af 4a. Acidification of these solutions with 2 M HCl caused a further shift to λ_{max} 262 nm as the open-chain anions were removed by conversion to 3, and the pure absorption of 4a remained. Prolonged heating of weakly acidic solutions of 4a caused loss of ultraviolet absorption, presumably owing to formation of 6.

Solutions of 3 in 0.2 M citrate-phosphate buffers were heated at 100 °C during 3 min and acidified, and the amounts of 4a formed were estimated by comparison of intensites of the UV absorption maxima at 262 nm. The amounts of decarboxylation product generated at pH 1 (0.1 M HCl), pH 4, and pH 6 were respectively about $^1/_6$, $^1/_2$, and $^1/_5$ of the amount generated at pH 3.

Heating neat 3 a few degrees above its melting point gave 2,5-dihydro-5-oxo-2-furanacetic acid (6); mp 108-110 °C (after recrystallization from ether-petroleum ether) (lit.[17] mp 110.5-111.5 °C); IR (KBr) 3300-2500 (m), 1790 (s), 1760 (s), 1700 (s), 1600 (w) cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 2.69 (HαA), 2.87 (HαB), 5.44 (H2), 6.16 (H4), 7.79 (H3) ($^2J_{\alpha A,\alpha B}$ = 16.5 Hz, $^3J_{2,\alpha A}$ = 7.5 Hz, $^3J_{2,\alpha B}$ = 5.8 Hz, $^3J_{2,3}$ = 1.5 Hz, $^3J_{3,4}$ = 5.5 Hz, $^4J_{2,4}$ = 2.0 Hz).[13,18]

Acknowledgment. This work was supported in part by a fellowship from the Danish Natural Science Research Council to J.W.J.

Registry No. 1a, 81158-33-0; 1b, 82639-54-1; 1c, 56549-11-2; 1c trisodium salt, 82639-55-2; 2a, 82639-56-3; 2b, 82639-57-4; 2c, 82639-58-5; 3, 82639-59-6; 4a, 1119-73-9; 4b, 82639-60-9; 5, 6666-46-2.

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Photodimerization of Coumarin in Aqueous and Micellar Media

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The photochemical and photophysical processes of many organic compounds are a function of the environment in which they are present. In this connection we have chosen to investigate the environmental perturbations on the

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