Table II. NOE and T_1 Values of Pyruvic Acid[a] and 2,2-Dihydroxypropanoic Acid in D_2O

C atom	T_1, s	NOE
Pyruvic Acid		
C_{CH_3}	3.75	3.0
C_α	36.16	2.3
C_{COOH}	38.08	1.32
2,2-Dihydroxypropanoic Acid		
C_{CH_3}	3.22	1.57
C_α	28.20	1.33
C_{COOH}	31.68	0.90

[a] Pyruvic acid, 0.5 M in D_2O; pD 0.9; T = 300 K.

Table III. Correlation Times and Rotation Barriers for the Methyl Groups of Pyruvic Acid and 2,2-Dihydroxypropanoic Acid Calculated for the Isotropic Approximation Case of the Woessner Equation

	pyruvic acid	2,2-dihydroxypropanoic acid
overall correlation time of the methyl group, s	4.16×10^{-12}	1.40×10^{-12}
correlation time for the lattice molecule, s	15.57×10^{-12}	5.78×10^{-12}
overall diffusions coefficient, s^{-1}	4.00×10^{10}	11.88×10^{10}
diffusion coefficient for the lattice molecule, s^{-1}	10.70×10^{9}	28.83×10^{9}
inner diffusion coefficient of the methyl group, s^{-1}		
(a) stochastic diffusion	1.37×10^{11}	1.55×10^{12}
(b) methyl jump	2.00×10^{11}	2.14×10^{12}
rotation barrier for the methyl group, kJ/M		
(a) stochastic diffusion	10.4	4.3
(b) methyl jump	10.5	4.5

α-carbon and the carboxyl carbon. This is an additional argument for the existence of an intramolecular hydrogen bond in α-keto acids in aqueous solution.

Although intermolecular hydrogen bonding with the solvent should compete strongly with intramolecular bonding, such intramolecular hydrogen bonds in aqueous solution have been established in such molecules as cyclic nucleotides by thermodynamic and kinetic measurements.[15] ^{13}C NMR has established intramolecular hydrogen bonding in α-keto acids as yet only in nonpolar solvents. Our investigations show that NMR observations of the α-carbon of such acids in aqueous solution also indicate the formation of an intramolecular hydrogen bond, in particular by chemical shift changes and NOE.

Table II contains NOE factors and spin-lattice relaxation times T_1 of pyruvic acid and 2,2-dihydroxypropanoic acid. These data can be used to determine correlation times and rotation barriers of the methyl groups and therefore to characterize the mobility of these molecules. The method of Woessner[16,17] was applied to both acids for an isotropic approximation (Table III), using structural data from the literature.[18] The calculated values suggest limited mobility of the pyruvic acid molecule, indicated by a larger overall correlation time and a higher rotation barrier for the methyl group. This effect can be due in part to hyperconjugation of the methyl group with the π electrons of the carbonyl-carboxyl system. On the other hand, 2,2-dihydroxypropanoic acid appears to have a relatively high mobility. This result is not in agreement with that of Patting and Strehlow,[9] who infer a limited mobility of 2,2-dihydroxypropanoic acid from ^1H NMR line width measurements.

(15) Bolton, P.; Vearns, D. *J. Am. Chem. Soc.* **1979**, *101*, 479.
(16) Woessner, D. E. *J. Chem. Phys.* **1962**, *37*, 647.
(17) Lambert, J. B.; Nienhuis, R. J.; Keepers, J. W. *Angew. Chem.* **1981**, *93*, 553.
(18) Marstokk, K. M.; Mollendal, H. *J. Mol. Struct.* **1974**, *20*, 257.

Experimental Section

NMR spectra were obtained on a WP 200 spectrometer with samples at the normal probe temperature of 300 K at 50.32 MHz for ^{13}C. Spectra were recorded with broad band decoupling except those with inverse gated decoupling. Spin-lattice relaxation times were determined by the inversion recovery procedure with eight τ values. NOEs were calculated from the difference of integrals of ^{13}C peaks from spectra with broad band decoupling and spectra with inverse gated heterodecoupling. Under the conditions chosen the acids were essentially undissociated. Chemical shifts were referred to external TMS. Measurements of pH were made with a Radiometer Model 26 pH meter. The calculation of pD values was performed according to Wüthrich.[19]

$$pD = pH \text{ (meter reading)} + 0.40$$

Prior to the NOE and T_1 experiments, samples were degassed by five pump-freeze-thaw cycles.

Pyruvic acid was purchased from Fluka and freshly distilled. (4-Methylphenyl)glyoxylic acid was prepared according to Schellenberger.[13]

(19) Wüthrich, K. *NMR in Biological Research: Peptides and Proteins*; North-Holland: Amsterdam, 1976.
(20) Schellenberger, A.; Fischer, G.; Oehme, G. *Chem. Ber.* **1967**, *100*, 425.

Benzocyclopropene-*p*-quinone: Generation and Trapping

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Benzoquinones fused with small rings provide interesting insight into the effects of strain on the physicochemical properties of quinone systems and also have potential utility as synthetic intermediates. Although benzocyclobutenequinones have been synthesized,[1] no synthesis of the more highly strained benzocyclopropenequinones has been described. We here report the pyrolytic generation and trapping of benzocyclopropene-*p*-quinone (**1**).[2]

In view of the electrophilic nature of quinones and the enhanced Diels-Alder reactivity of the moderately strained benzocyclobutene-*p*-quinone (**2**) as a dienophile, the more highly strained quinone **1** should be a very reactive compound, particularly toward nucleophiles. On the other hand, **1** could be expected to be thermally, reasonably stable because it cannot undergo a symmetry-allowed, unimolecular thermal ring opening like that of the cyclobutene ring in **2**,[3,4] although ring opening of **1** by a radical mechanism may be possible with higher activation energy.

(1) (a) Horner, L.; Schmelzer, H. G.; Thomson, B. *Chem. Ber.* **1960**, *93*, 1774. (b) Rieke, R. D.; Rich, W. E.; Ridgway, T. H. *Tetrahedron Lett.* **1969**, 4381. (c) Oda, M.; Kanao, Y. *Chem. Lett.* **1981**, 37. (d) Kanao, Y.; Iyoda, M.; Oda, M. *Tetrahedron Lett.* **1983**, *24*, 1727. (e) Iyoda, M.; Yamauchi, T.; Oda, M. *Synthesis* **1986**, 303.
(2) Systematic nomenclature: bicyclo[4.1.0]hepta-1(6),3-diene-2,5-dione.
(3) Kanao, Y.; Oda, M. *Bull. Chem. Soc.* Jpn. **1984**, *57*, 615.
(4) Compound **1** might undergo an intermolecular ene reaction to give a dimer, as does cyclopropene.

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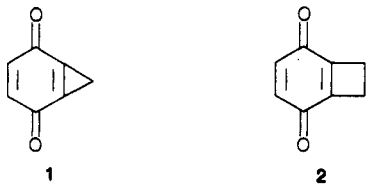
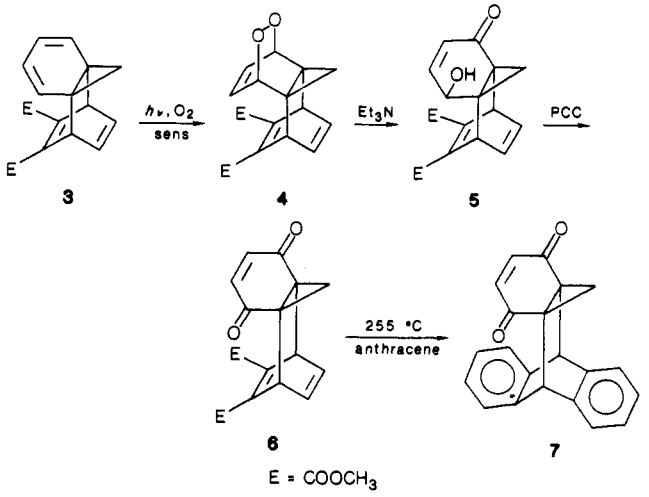
Chart I



1 2

Chart II



3 4 5 6 7

Accordingly, we have examined the pyrolytic generation of **1** through a symmetry-allowed retro-Diels–Alder reaction.

Photosensitized oxygenation of the tetracyclic 1,3-diene **3**[5] in acetone using hematoporphyrin as a sensitizer gave the epidioxide **4** as the sole product in 93% yield (69% conversion). Although the stereochemistry of **4** could not be determined spectroscopically, the high stereoselectivity in the reaction indicates that singlet oxygen adds exclusively from the less hindered side of **3**. Treatment of **4** with triethylamine at room temperature gave the hydroxy enone **5** (96% yield), which in turn afforded the enedione **6** upon oxidation with pyridinium chlorochromate (93% yield). The mass spectrum of **6** shows a base peak at m/z 163, which corresponds to the mass of dimethyl phthalate minus one methoxy group; the peak corresponding to **1** (m/z 120) is weak (9%).

Flash vacuum pyrolysis of **6** at 400 °C gave little reaction but was almost complete at 500 °C. Although dimethyl phthalate was formed in good yields, the desired quinone **1** did not reach the cold trap. Instead, a considerable amount of yellow-brown film (IR 1720–1740 cm^{-1}, br) was formed on the wall inside the quartz pyrolysis tube midway to the trap.

We succeeded in trapping **1** as a Diels–Alder adduct by conducting the pyrolysis of **6** in molten anthracene. A mixture of **1** and anthracene (3 equiv) was heated in a glass tube at 255 °C for 10 min to give the exchanged Diels–Alder adduct **7** in 12% yield in addition to dimethyl phthalate (16%) and recovered **6** (41%). The yield of **7** was sensitive to conditions; both higher temperatures and longer reaction times decreased the yield because **7** decomposes above 210 °C. The selective cycloaddition of **1** to anthracene at the constrained internal double bond to form **7** parallels the Diels–Alder reaction of **2** with 1,3-dienes.[6] Attempts to trap **1** with other dienes such as tetraphenylcyclopentadienone or 9,10-dimethylanthracene under similar conditions resulted only in extensive decomposition.

In conclusion, although benzocyclopropene-*p*-quinone can be generated pyrolytically, it appears to be a highly reactive substance because of severe strain. It might be possible to generate **1** by pyrolysis of the analogue of **6** without the carbomethoxy groups and to isolate it by trapping in a frozen matrix.

(5) Vogel, E.; Grimme, W.; Korte, S. *Tetrahedron Lett.* **1965**, 3625.
(6) Oda, M.; Kanao, Y. *Chem. Lett.* **1981**, 1547.

Experimental Section

Melting points were taken on a Mettler FP2 apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi EPI-G3 grating spectrophotometer. ^1H NMR spectra were taken on a Varian XL-100 or a JEOL PMX-60SI spectrometer, and mass spectra were obtained on a JEOL JMS-01SG-2 instrument.

Photooxygenation of Dimethyl Tetracyclo[6.2.2.1^{2,7}.0^{2,7}]-trideca-3,5,9,11-tetraene-9,10-dicarboxylate (3). A solution of **3** (1.18 g, 4.15 mmol) and hematoporphyrin (20 mg) in acetone (140 mL) was placed in a long Pyrex glass vessel (20 × 500 mm) equipped with a condensor and a narrow Teflon tube for gas inlet, and, under bubbling oxygen, irradiated externally with five surrounding 20-W fluorescent lamps at room temperature for 11 h. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel, eluting with benzene–ethyl acetate (9:1 v/v). Unchanged **3** (360 mg, 30.5%) and the epidioxide **4** (851 mg, 65%; 93% based on recovery) were obtained in the order of elution. Recrystallization of the latter from ethanol gave colorless crystals: mp 88 °C dec; IR (KBr) ν_{max} 1722, 1707, 1630, 1598, 1288, 1111, 1064 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.52 (1 H, d, J = 6.5 Hz), 0.89 (1 H, d, J = 6.5 Hz), 3.69 (6 H, s), 4.16 (2 H, m), 4.81 (2 H, m) 6.24 (4 H, m). Anal. Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10. Found: C, 64.56; H, 5.13.

Reaction of 4 with Triethylamine. To a water-cooled solution of the epidioxide **4** (850 mg, 2.7 mmol) in dichloromethane (20 mL) was added dropwise triethylamine (1 mL). The solution was stirred for 1 h, the solvent evaporated, and the residue chromatographed on silica gel using benzene–ethyl acetate (7:3) as eluent to give the keto alcohol **5** (819 mg, 93%) as a solid. Recrystallization from benzene gave colorless prisms: mp 150–151 °C; IR (KBr) ν_{max} 3415, 1734, 1717, 1656, 1630, 1620, 1598, 1292, 1240, 1068 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.07 (1 H, d, J = 6.5 Hz), 1.46 (1 H, d, J = 6.5 Hz), 2.70 (1 H, br, OH), 3.77 (6 H, s), 4.40 (2 H, m), 4.56 (1 H, br), 4.78 (2 H, m), 5.86 (1 H, d, J = 10.0 Hz), 6.31 (2 H, m) 6.53 (1 H, dd, J = 10.0 Hz). Anal. Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10. Found: C, 64.69; H, 5.08.

Oxidation of 5. To a solution of the keto alcohol **5** (819 mg, 2.6 mmol) in dichloromethane (26 mL) was added portionwise pyridinium chlorochromate (840 mg, 3.9 mmol) under stirring at room temperature. The mixture was further stirred for 2 h, filtered, concentrated, and chromatographed on silica gel to give the enedione **6** (760 mg, 93%) as a pale yellow solid. Recrystallization from benzene–hexane gave pale yellow prisms: mp 149–150 °C; IR (KBr) ν_{max} 1728, 1707, 1675, 1632, 1598, 1593, 1290, 1268, 1056, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.85 (1 H, d, J = 6.5 HZ), 2.03 (1 H, d, J = 6.5 Hz), 3.72 (6 H, s), 4.84 (2 H, m), 6.37 (2 H, m), 6.42 (2 H, s); MS (75 eV) m/z (relative intensity) 314 (M^+, 50), 283 (36), 255 (38), 194 (18), 163 (100), 120 (9). Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found C, 64.75; H, 4.53.

FVP of 6. The enedione **6** (100–200 mg) was placed in the reservoir of the pyrolysis apparatus (quartz glass, 15 × 400 mm) packed with quartz chips and equipped with an electric furnace (L = 300 mm) preheated to 400–500 °C. The dione was slowly evaporated at 0.5 mmHg by using a heat gun and the pyrolysate was led into a cold trap immersed in a dry ice–acetone bath. Only dimethyl phthalate reached the cold trap; the unchanged **6** and a yellow-brown film condensed inside the glass tube midway to the trap.

Trapping of Benzocyclopropene-*p*-quinone (1) with Anthracene. A solid mixture of the enedione **6** (32 mg, 0.10 mmol) and anthracene (54 mg, 0.30 mmol) was sealed in a Pyrex glass tube (8 × 100 mm) under vacuum. The tube was inserted into the hot zone of an electric furnace preheated at 255 °C and kept there for 10 min. The reaction mixture was separated by preparative TLC (SiO_2, C_6H_6) to give the exchanged enedione **7** (3.5

mg, 12%), dimethyl phthalate (3.1 mg, 16%), and **6** (13 mg, 41%). Recrystallization of **7** gave pale yellow prisms: mp 216 °C dec; IR ($CDCl_3$) ν_{max} 1672 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.10 (1 H, d, J = 6.0 Hz), 2.00 (1 H, d, J = 6.0 Hz), 5.17 (2 H, s), 6.32 (2 H, s), 6.95–7.50 (8 H, m); MS (7.5 eV), m/z (relative intensity) 298 (M^+, 86), 216 (86), 215 (100), 178 (28). Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.22; H, 4.86.

Electrochemical Transformations of Aldehydes into Methyl Carboxylates and Nitriles

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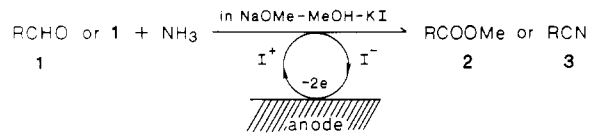
The one-step transformation of aldehydes (**1**) into the corresponding methyl carboxylates (**2**) or nitriles (**3**) appears to be an attractive synthetic process. Although several methods have been reported for the direct preparation of **2** from **1**,[1] or **3** from **1** with ammonia,[2] they usually require large amounts of reagents, elevated temperature, and/or a lengthy reaction period. We describe in this paper an efficient procedure for obtaining **2** or **3** from **1** by means of indirect electrooxidation using a redox system of iodide ions as a mediator.[3]

Results and Discussion

The electrooxidative preparation of **2** from **1** was conducted in MeOH containing NaOMe and a catalytic amount of KI, whereas for the preparation of **3** excess ammonia was further added to the electrolyte system. All



of the electrolyses were carried out in a divided cell with a platinum anode under a constant current until a yield of desired product reached its maximum value. The results of electrolyses are summarized in Table I.

Preparation of 2. As shown in the table, this method gave good results with aromatic aldehydes. In each case, almost all of the quantity of **1** was converted into **2** at the stage where the theoratical amount of electricity (2 F/mol of **1**) has passed through. The yield of the substituted methyl benzoates was hardly affected by the steric and electronic effects of the substituents. Aliphatic aldehydes having an α-hydrogen atom were not applicable, because of aldol condensation.

An exellent catalytic behavior was also observed with NaI, $(Et)_4NI$, and I_2, but other alkali halide such as KBr or KCl did not show their effects for converting **1** into **2**. The presence of NaOMe as a strong base and the separation of the anolyte from catholyte were essential in order to obtain satisfactory yields of **2**. For example, the electrolysis with benzaldehyde in an undivided cell gave only about a 48% yield of methyl benzoate even when 0.5 equiv of KI for **1** was used, and no **2** was formed when the electrolysis was carried out without NaOMe in a divided cell by using a neutral salt such as $NaClO_4$ or $(Et)_4OTs$ as the supporting electrolyte together with KI. In these cases, the dimethyl acetal of **1** was formed. Probably, the corresponding acid generated at the anode and catalyzed the acetal formation.

Table I. Electrochemical Transformation of Aldehydes into Methyl Carboxylates[a] or Nitriles[b]

RCHO, R	electricity passed, F/mol	yield of ester,[c] %	electricity passed, F/mol	yield of nitrile,[c] %
C_6H_5	2.0	80	2.5	73
2-$CH_3C_6H_4$	2.2	84	2.6	86
4-$CH_3C_6H_4$	2.1	82	2.6	90
2-$CH_3OC_6H_4$	2.6	78	2.8	70
4-$CH_3OC_6H_4$	2.1	86	2.8	90
2-ClC_6H_4	2.2	83	2.6	88
4-ClC_6H_4	2.0	87	2.2	85
2-$NO_2C_6H_4$	2.1	70	2.0	0[f]
4-$NO_2C_6H_4$	2.0	91	2.0	0[f]
2-furyl	2.0	70	2.2	trace[d]
1-naphthyl	2.1	84	2.4	54
$(CH_3)_2(HOCH_2)C$	2.0	68	2.2	55
n-C_3H_7			3.3	59[e]
n-C_5H_{11}			3.0	50
n-C_7H_{15}	2.0	0[f]	2.2	66
$CH_3(CH_2)_3(C_2H_5)CH$	2.0	0[f]	3.0	70
cyclo-C_6H_{11}			2.1	48

[a] Anolyte: aldehyde (50 mmol) and KI (5 mmol) in MeOH (80 mL) containing NaOMe (10 mmol). Constant current: 0.5 A. Temperature: ca. 17 °C. [b] Anolyte: aldehyde (50 mmol), KI (10 mmol), and NH_3 (380 mmol) in MeOH (80 mL) containing NaOMe (10 mmol). Constant current: 0.5 A. Temperature: ca. 5 °C. [c] Isolated yield based on **1**. [d] Methyl furimidate was obtained in a yield of 60%: bp 67–69 °C (19 mm); IR (neat) 3320 (NH), 1655 cm^{-1} (C=NH); ^1H NMR ($CDCl_3$) δ 3.91 (s, 3, OCH_3), 6.47 (dd, 1, J = 3 Hz, furan ring), 6.78 (dd, 1, J = 3 Hz, furan ring), 7.50 (dd?, 1, furan ring), 7.71 (s, 1, NH); MW 125 (mass). [e] Determined by GLC. [f] Unidentified products were formed.

In material yield, current efficiency, and ease of experimental manipulation, the present method was superior to our previous one using a NaCN–MeOH electrolyte system.[1]

Preparation of 3. Analogously, the electrochemical preparation of **3** was successfully performed with aromatic aldehydes in the presence of excess ammonia. To suppress the formation of undesirable **2**, a large excess of ammonia and a small amount of NaOMe were used. Under the present condition, no or little **2** was formed in most cases.

From furfural, methyl furimidate was obtained as the main product along with a small amount of furonitrile. It is highly probable that the produced furonitrile was solvolyzed with MeOH in the presence of NaOMe. In fact, furonitrile was readily converted into methyl furimidate by treatment with NaOMe–MeOH at room temperature.[4] Nitrobenzaldehydes afforded intractible mixtures, which did not contain the expected **3**.

With similar ease, aliphatic aldehydes could also be transformed into **3**, although in somewhat lower yields. The decrease in the yield may be partly ascribed to an aldol condensation. In these cases, highly viscous liquids remained after distillation of the products.

Thus, it can be said that a catalytic amount of KI promoted both transformation reactions. In these electrolyte systems, the iodide anion is most readily electrooxidized,[5]

(1) For our previous report on the electrooxidative conversion of **1** into **2**, see: Chiba, T.; Okimoto, M.; Nagai, H.; Takata, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 335 and references cited therein.

(2) (a) Parameswaren, K. N.; Friedman, O. M. *Chem. Ind. (London)* **1965**, 988. (b) Brackman, W.; Smit, P. J. *Recl. Trav. Chim. Pay-Bas* **1963**, *82*, 757. (c) Misono, A.; Osa, T.; Koda, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 854. (d) Nakagawa, K.; Onoue, H.; Minami, K. *J. Chem. Soc., Chem. Commun.* **1966**, 17. See also: Ganboa, I.; Palomo, C. *Synth. Commun.* **1983**, *13*, 219.

(3) For a review of oxidation using halide ion as the mediator, see: Shono, T. *Tetrahedron* **1984**, *40*, 811.

(4) For example, see: Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic: New York, 1972; Vol. 3, Chapter 8.

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