for 15 h with a $CaCl_2$ drying tube in place. The solution was cooled and filtered and the solvent removed on a rotary evaporator. The residue, an oil, was distilled under vacuum, giving **2**: bp 80–90 °C (0.07 torr); 31.8 g (97%); ^1H NMR ($CDCl_3$) δ 3.34 (s, 6 H), 3.90 (s, 3 H), 6.05 (s, 1 H) 7.3–7.9 (m, 4 H); IR (neat) 1723 (C=O), 1289, 1258, 1195, 1134, 1104, 1065 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.73; H, 6.35.

In the absence of trimethyl orthoformate, the NMR spectrum of the reaction product showed that it consisted of **2** and two other products.

2-(Dimethoxymethyl)benzyl Alcohol (3). To a slurry of 3.8 g of LAH in 300 mL of dry ether (distilled from Na) was added 31.8 g (0.15 mol) of **2** dropwise with stirring. The mixture was stirred at room temperature for 12 h. After hydrolysis with water, the decanted ether solution was dried ($MgSO_4$), filtered, and concentrated at less than 40 °C. An NMR spectrum of the residue (27 g, 98%) showed it to be essentially pure **3**, and it can be distilled: bp 98–106 °C (1.25 torr); 22.9 g (83%); decomposition during distillation was sometimes a problem; ^1H NMR ($CDCl_3$) δ 3.33 (s, 6 H), 3.33 (obscured t, J = 6 Hz, 1 H, exchanges with D_2O), 4.68 (d, J = 6 Hz, 2 H), 5.48 (s, 1 H), 7.1–7.6 (m, 4 H); IR (neat) 3050–3650 (br OH), 2920, 1180, 1103, 1078, 1040, 745 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.81; H, 7.86.

1-Methoxyphthalan (4a). To 200 mL of absolute methanol were added 10 g (0.055 mol) of crude 2-(dimethoxymethyl)benzyl alcohol (**3**) and 5 g of Dowex 50W-X8 resin. The mixture was stirred for 12 h at room temperature with a drying tube in place. The solution was filtered, and the solvent was removed with a rotary evaporator by using a cool water bath. The residual oil (7.8 g, 95%) had an NMR spectrum identical with that reported.[6]

1-Ethoxyphthalan (4b) was prepared by using **3** and absolute ethanol in the manner described for **4a**. The crude product, an oil (95%), had an NMR spectrum identical with that reported.[7]

Attempts to distil either **4a** or **4b** led to extensive polymerization.

1,4-Anthraquinone (10). To 50 mL of glacial acetic acid and 10 mL of water were added 1.6 g (8.8 mmol) of **3** and 1.1 g (10 mmol) of *p*-benzoquinone. The mixture was stirred at 100 °C for 10 h. The solution was cooled and poured into water, and the resulting solid was filtered, dissolved in chloroform, heated with decolorizing charcoal, and filtered. Removal of the solvent left a solid red residue which was recrystallized from ethanol, giving **10**: 0.46 g (25%); mp 218–221 °C dec (lit.[8] mp 219–223 °C); NMR ($CDCl_3$) δ 7.07 (s, 2 H), 7.6–7.8 (m, 2 H), 8.0–8.2 (m, 2 H), 8.63 (s, 2 H); IR (Nujol) 1679 (C=O), 1628, 1613, 1311, 859 cm^{-1}.

Pentacene-6,13-quinone (11). To 1.5 g (8.2 mmol) of **3** were added 50 mL of glacial acetic acid, 10 mL of water, and 0.35 g (3.2 mmol) of *p*-benzoquinone. After the mixture was heated 12 h at 100 °C, the yellow-orange precipitate was filtered from the reaction mixture and recrystallized from glacial acetic acid: 0.55 g (55%); mp 382–384 °C (lit.[9] mp 388–389 °C); IR (KBr) 1678 (C=O), 1397, 1282, 1191, 992, 766 cm^{-1}; NMR (Me_2SO-d_6) δ 7.7–8.0 (m, 4 H), 8.3–8.6 (m, 4 H), 9.0 (s, 4 H).

Tetracene-5,12-quinone (9). The above procedure for **11** was repeated by using (5.5 mmol) of **3** and 3 g (19 mmol) of steam-distilled 1,4-naphthoquinone. The **9** which precipitated, recrystallized from glacial acetic acid, amounted to 1 g (70%) of a yellow-brown solid: mp 289–291 °C (lit.[8] mp 290–292 °C); NMR (Me_2SO-d_6) δ 7.7–8.1 (m, 4 H), 8.2–8.5 (m, 4 H), 8.88 (s, 2 H). The IR spectrum was identical with that in the Aldrich collection.

1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-*endo*,*cis*-2,3-dicarboxylic Acid (7). To 50 mL of 85% aqueous acetic acid were added 3 g (17 mmol) of **3** and 1.6 g (16 mmol) of maleic anhydride. The mixture was heated at 100 °C with stirring for 10 h. The solvent was then removed on a rotary evaporator and the residue, an oil, dissolved in benzene. Upon cooling there was obtained 1.9 g (54%) of crystalline **7**: mp 171–172 °C (acetonitrile); NMR (Me_2SO-d_6) δ 3.50 and 3.54 (AA'XX' dd, J = 2, 3 Hz, 2 H), 5.44 and 5.48 (AA'XX' dd, J = 2, 3 Hz, 2 H), 6.9–7.4 (m, 4 H), 11.9 (br s, 2 H); IR (Nujol) 2500–3400 (br OH), 1708 and 1741 (C=O), 1193, 966, 902, 852, 751, 693 cm^{-1}.

The compound was characterized by recrystallization from acetic anhydride to give the anhydride of *endo,cis*-1,4-epoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid: mp 172–173 °C (lit.[3] mp 172 °C); NMR (Me_2SO-d_6) 4.15 and 4.20 (AA'XX' dd, J = 2, 4 Hz, 2 H), 5.86 and 5.91 (AA'XX' dd, J = 2, 4 Hz, 2 H), 7.32 (s, 4 H); IR (Nujol) 1850 and 1775 (C=O), 1281, 1221, 1077, 984, 916 cm^{-1}.

2,3-Dicarbomethoxy-1,4-epoxy-1,4-dihydronaphthalene (6). To 5 mL of glacial acetic acid and 2 mL of water were added 1 g (5.5 mmol) of crude **3** and 3 g (21 mmol) of dimethyl acetylenedicarboxylate. The solution was stirred at room temperature for 2.5 h and then at 100 °C for 10 h. The solvent was removed to give 1 g (80%) of crude **6**, an oil, whose NMR spectrum exhibited only those peaks characteristic of the desired product. Distillation of **6** [bp 170–174 °C (1.0 torr)] was accompanied by decomposition and did not improve the quality of the product: NMR ($CDCl_3$) δ 3.80 (s, 6 H), 5.96 (s, 2 H), 7.0–7.6 (m, 4 H); IR (neat) 1730 (C=O), 1440, 1220, 1118, 860, 760 cm^{-1}. The compound was characterized by conversion to *endo,cis*-2,3-dicarbomethoxy-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (**12**) by catalytic hydrogenation. To 30 mL of ethyl acetate were added 2.6 g (11 mmol) of crude **6** and 0.4 g of 5% Pd/C. The hydrogenation was effected by using a Parr hydrogenator under 60 psi of H_2 gas for 10 h. After filtration and removal of the solvent, 10 mL of methanol was added, whereupon 2 g (77%) of **12** crystallized MP 102-104°C (aqueous MeOH) (lit.[10] mp 105 °C); NMR ($CDCl_3$) δ 3.45 (s, 6 H), 3.6 and 3.63 (AA'XX' dd, J = 2, 3 Hz, 2 H), 5.46 and 5.50 (AA'XX' dd, J = 2, 3 Hz, 2 H), 7.1–7.4 (m, 4 H); IR (Nujol) 1727 and 1713 (C=O), 1296, 1262, 1182, 1076 cm^{-1}.

***trans*-2,3-Dicarbomethoxy-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (8).** To 5.0 g (28 mmol) of **3** were added 50 mL of glacial acetic acid and 4 g (28 mmol) of dimethyl fumarate. After the mixture was heated at 100 °C for 12 h, the solvent was removed on a rotary evaporator, leaving a viscous oil whose NMR spectrum showed it to be essentially pure **8**. The oil resisted crystallization until seeded with crystalline **8** from another source.[11] It was recrystallized from heptane, giving **8**: 6.3 g (70%); mp 66–67 °C (lit.[10] mp 66 °C). Spectral properties were identical with those obtained from another source.[11]

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Registry No. **1**, 119-67-5; **2**, 87656-31-3; **3**, 87656-32-4; **4a**, 67536-29-2; **4b**, 75802-19-6; **6**, 85828-01-9; **7**, 87656-33-5; **8**, 26580-83-6; **9**, 1090-13-7; **10**, 635-12-1; **11**, 3029-32-1; **12**, 26580-84-7; MA, 108-31-6; DMAD, 762-42-5; DF, 624-49-7; *p*-benzoquinone, 106-51-4; 1,4-naphthoquinone, 130-15-4.

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Pyrolysis of Pyruvic Acid in the Gas Phase. A Study of the Isomerization Mechanism of a Hydroxycarbene Intermediate

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Hydroxy- and alkoxycarbenes have been suggested as key intermediates in the photochemistry of aldehydes and ketones.[1] However, little is known about the structure

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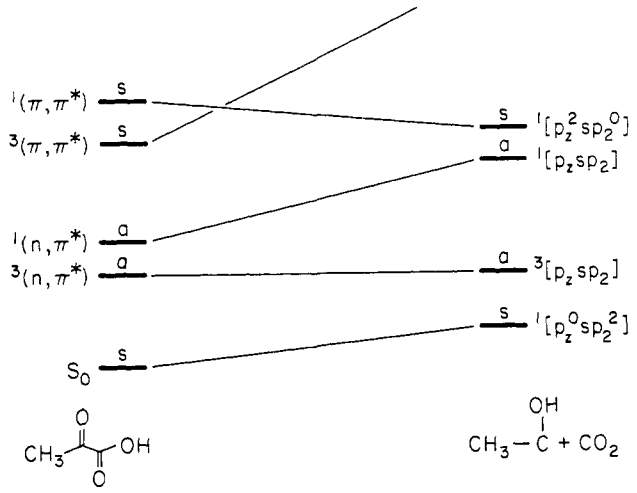
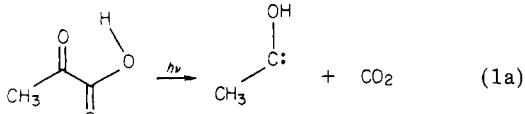


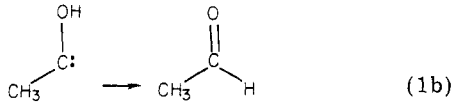
Figure 1. State correlation diagram for the decarboxylation of pyruvic acid to yield a hydroxycarbene product. s and a denote states that are symmetric and antisymmetric with respect to a mirror plane in which all heavy nuclei are assumed to lay.

or reactivity of these species. While hydroxymethylene is believed to isomerize to formaldehyde via a [1,2] hydrogen shift from oxygen to carbon, alkyl-substituted hydroxycarbenes *a priori* might isomerize via hydrogen shifts from oxygen and/or from carbon. We report here an isotope labeling experiment that addresses this point and indicates that the oxygen to carbon hydrogen shift is the more facile.

We have previously studied the photochemical decarboxylation of pyruvic acid in the gas phase[2] and found evidence that CO_2 is formed in concert with a hydroxycarbene that undergoes subsequent isomerization to acetaldehyde (eq 1). We have found the gas-phase pyrolysis

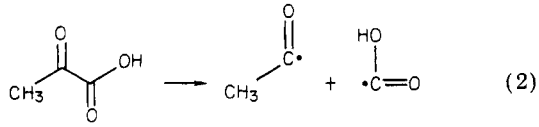


(1a)



(1b)

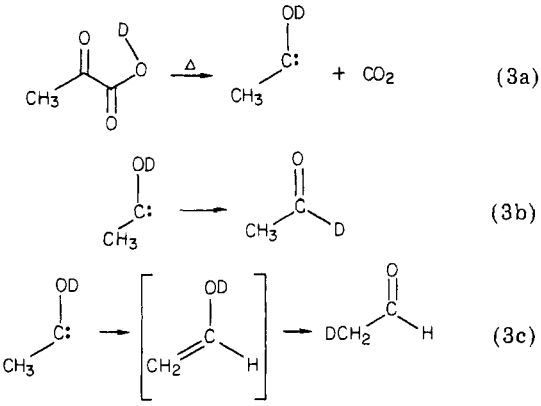
of pyruvic acid also yields acetaldehyde and CO_2 as the major products. This suggests that a similar mechanism is operative in both experiments. A free-radical mechanism, eq 2, should result in the formation of significant



(2)

amounts of CH_4 and CO. These species are not observed, indicating the relative unimportance of mechanism 2 in the pyrolysis of pyruvic acid. A state correlation diagram can be constructed[3] for mechanism 1a (see Figure 1). The diagram indicates that hydroxycarbene formation is symmetry allowed from either the ground state, S_0, or the lowest triplet state,[3] (n,π^*), of pyruvic acid and provides additional evidence for a common mechanism in the thermal and photochemical decarboxylations. Although it is possible that CO_2 and acetaldehyde might be formed directly in the pyrolysis of pyruvic acid, the resulting four-center transition state would be highly strained, suggesting that the five-center transition state associated with the symmetry-allowed reaction is more plausible.

The isomerization of the hydroxycarbene to acetaldehyde, eq 1b, might proceed via a hydrogen shift from the methyl group *or* the hydroxyl group. These two possibilities can be differentiated via a deuterium-labeling experiment, eq 3. An oxygen to carbon deuterium shift



(3a)

(3b)

(3c)

should yield acetaldehyde-*1-d*, CH_3CDO, whereas a carbon to carbon hydrogen shift should yield acetaldehyde-*2-d*, DCH_2CHO, via the tautomerization of the vinyl alcohol-*O-d* intermediate. The pyrolysis of pyruvic acid-*O-d* in the gas phase yields CH_3CDO exclusively, within experimental error (i.e., >90%). This was determined by gas-phase IR spectroscopy[4] of the reaction products, which shows a strong absorption at 2050 cm^{-1} (aldehydic C–D). No absorption was observed in the 950–1000-cm^{-1} range. Absorption in this range corresponds to the CCD bending and CH_2D deformation modes of DCH_2CHO. In the case of authentic DCH_2CHO, these bands are observed to have an intensity ca. one-third that of the aldehydic C–H stretch.[4] We observed a small absorption at 2750 cm^{-1}, corresponding to an aldehydic C–H stretch, but control experiments demonstrate that this arises due to isotope exchange of pyruvic acid-*O-d* in the pyrolysis tube. This isotope exchange results in some CH_3CHO being isolated in the pyrolysate. We conclude that no DCH_2CHO is formed in the pyrolysis of pyruvic acid-*O-d* and that the hydroxycarbene generated via this pyrolysis isomerizes via mechanism 3b.

This finding can be interpreted in terms of the results of ab initio theoretical studies of carbene isomerization barriers. Ample experimental and theoretical evidence[5] suggests a negligible barrier for the ethylidene–ethylene isomerization eq 4. The isomerization of hydroxymethylene to formaldehyde, eq 5, is, by contrast, predicted to have a barrier[6] of ca. 36 kcal/mol. Thus, one might

$$CH_3-\ddot{C}H \rightarrow CH_2=CH_2 \quad (4)$$

$$H-\ddot{C}-OH \rightarrow H_2C=O \quad (5)$$

assume that mechanism 3c should be facile relative to mechanism 3b, but such an assumption discounts the impact of any substituent effect by the hydroxyl group on

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the barrier to C–H migration. In fact, a significant substituent effect might be anticipated in light of the observation by Moss and co-workers[7] that methylchlorocarbene, $CH_3\ddot{C}Cl$, undergoes addition to olefins in competition with unimolecular isomerization to vinyl chloride. By contrast, the methyl group in $CH_3\ddot{C}OH$ is expected to have little effect on the barrier to O–H migration. This is consistent with our data. Our observation of ≥90% O–H migration indicates that the barrier to C–H migration must exceed that for O–H migration by at least 3.3 kcal/mol.

We are presently attempting to spectroscopically characterize the carbene formed via mechanism 1a and to determine the isomerization kinetics for mechanism 1b. Chemical trapping of the carbene is also being investigated.

Experimental Section

NMR spectra were recorded on a Varian EM-390 spectrometer using $CDCl_3$ as a solvent with tetramethylsilane as an internal standard. IR spectra were recorded on a Beckman IR-8 or a Perkin-Elmer 180 spectrometer using 7–10-cm gas cells equipped with NaCl windows. Pyruvic acid was obtained from Aldrich Chemical Co. and was vacuum distilled prior to use. Pyruvic acid-*O-d* was prepared via deuterium exchange with D_2O and was determined to be 90% deuterated at oxygen by NMR.

Pyrolysis of Pyruvic Acid. Pyrolyses were accomplished by flash distilling pyruvic acid through a heated quartz tube (6-mm i.d., 15-cm heated length, 500 °C) under vacuum (pressure ~10 torr) and trapping the effluent at 77 K. We estimate residence times in the heated quartz tube to be ca. 10 ms. IR analysis of the effluent indicated the presence of CO_2 and CH_3CHO. NMR analysis after removal of the CO_2 indicated the presence of CH_3CHO. The extent of reaction was essentially quantitative.

Pyrolysis of Pyruvic Acid-*O-d*. Pyrolyses of pyruvic acid-*O-d* were accomplished as indicated above with the exception that prior to a sequence of 3–5 runs, D_2O was flash distilled through the pyrolysis system. The D_2O effluent was removed from the trap prior to the pyruvic acid-*O-d* pyrolyses. Products from these pyrolyses were analyzed by IR and NMR spectroscopy as indicated above. In a control experiment, pyruvic acid-*O-d* was flash distilled through the pyrolysis tube at a tube temperature of ca. 100 °C. Under these conditions, negligible pyrolysis was found to occur. The recovered pyruvic acid was determined by NMR to be ≥80% deuterated at oxygen.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. Pyruvic acid, 127-17-3; methylhydroxycarbene, 30967-49-8.

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A Regiospecific, Convergent Route to 2,3-Disubstituted Cyclopentanones†

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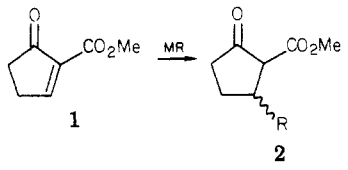
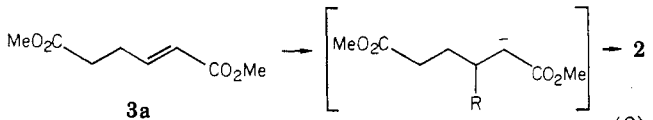
The 2,3-disubstituted cyclopentanones include many biologically active compounds, including the 11-deoxyprostaglandins[1] and the cyclopentanoid antibiotic antitumor agents such as sarkomycin.[2] A conceptually attractive route to these compounds begins with conjugate addition of organometallic reagents to enone **1**.[3] The resulting



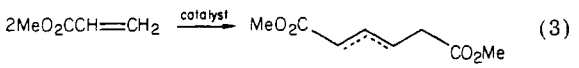
1 2 (1)

2-carbomethoxycyclopentanones can then be transformed by standard methods into a variety of useful cyclopentanoids. However, compound **1** is unstable, difficult to prepare, and polymerizes in the presence of many nucleophiles.[3b] It occurred to us that eq 2, a conjugate addition/cyclization utilizing dimethyl hex-2-enedioate, **3a**, would represent an attractive alternative to eq 1. Tandem conjugate addition/cyclization reactions related to eq 2 have been reported.[4] The practicality of this approach depends on the ready availability of **3a**, and therefore a high yield synthesis of **3a** by dimerization of methyl acrylate was first developed.



3a (2)

The catalytic tail-to-tail dimerization of methyl acrylate (eq 3) has been reported.[5] Unfortunately, we found that



(3)

Δ^2 isomer **3a**
Δ^3 isomer **3b**

each of the known catalysts had severe limitations for the practical synthesis of **3a**. In particular, predominant formation of isomeric **3b**, limited catalyst life, or further oligomerization of product dimers were problems. We have now discovered that the loosely coordinated cationic palladium complex $Pd(NCMe)_4(BF_4)_2$[6,7] affords very high yields of **3a** under mild conditions, particularly in the presence of anhydrous $LiBF_4$. Thus, treatment of neat methyl acrylate with 0.005 equiv of palladium catalyst[8] and 0.16 equiv of $LiBF_4$ at 40 °C for 30 h afforded after distillation a 93% yield of dimers consisting of 93–96% of the

† Contribution No. 3243.

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(7) For other organic transformations catalyzed by $Pd(NCMe)_4^{2+}$; see: Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627–4629.

(8) The amount of palladium catalyst can be further diminished by addition of a nonligating reoxidant such as benzoquinone (cf. ref 5c) or VOF_3.

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