s, 1 H), 6.22 (dd, J = 6.1, 1.5 Hz, 1 H), 7.27 (dd, J = 1.5, 6.3 Hz, 1 H).

Anal. Calcd for $C_{17}H_{36}O_4Si_2$: C, 58.02; H, 9.74. Found: C, 57.97; H, 9.64.

***c*-5-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-*t*-5-hydroxy-*r*-4-acetoxy-2-cyclopentenone (18b).** Application of general protocol C to ketone **19b** (47 mg, 0.16 mmol) gave a red syrup. This was purified via preparative TLC (9:1 CH_2Cl_2/Et_2O, R_f 0.38) to afford 26 mg (58%) of **18b** as a colorless oil possessing the following spectral data: IR ($CHCl_3$) 3540 (m, br), 3450 (m, br), 2960 (s), 2935 (s), 1725 (s), 1235 (s), 1140 (s), 990 (w), 860 (s), 835 (m) cm^{-1}; NMR (360 MHz, $CDCl_3$) δ 0.01 (s, 3 H), 0.02 (s, 3 H), 0.83 (s, 9 H), 2.12 (s, 3 H), 3.37 (br s, 1 H), 3.68 (AB q, J_{AB} = 9.9 Hz, 2 H), 5.74 (dd, apparent t, J = 1.5, 1.3 Hz, 2 H), 6.37 (dd, J = 1.5, 6.1 Hz, 1 H), 7.46 (dd, J = 1.8, 6.1 Hz, 1 H).

Anal. Calcd for $C_{14}H_{24}O_5Si$: C, 55.97; H, 8.05. Found: C, 56.06; H, 8.02.

***c*-5-(Acetoxymethyl)-*t*-5-hydroxy-*r*-4-[(*tert*-butyldimethylsilyl)oxy]-2-cyclopentenone (18c).** Application of general protocol C to ketone **19c** (55 mg, 0.18 mmol) gave a red syrup. The latter was purified via preparative TLC (9:1 CH_2Cl_2/Et_2O, R_f 0.42) to afford 17 mg (32%) of enone **18c** as pale yellow needles. An analytical sample was obtained via recrystallization (pentane, −20 °C; mp 77.5–79.0 °C) and possessed the following spectral data: IR 3550 (m), 3450 (m, br), 2950 (s), 2940 (s), 2870 (s), 1735 (s), 1470 (s), 1375 (s), 1120 (s), 1040 (m), 920 (w), 840 (s) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 0.15 (s, 6 H), 0.91 (s, 9 H), 2.04 (s, 3 H), 3.32 (br s, 1 H), 4.24 (AB q, J_{AB} = 12.3 Hz, 2 H), 4.78 (dd, apparent t, J = 1.5, 1.8 Hz, 1 H), 6.26 (dd, J = 1.5, 6.3 Hz, 1 H), 7.32 (dd, J = 1.8, 6.3 Hz, 1 H).

Anal. Calcd for $C_{14}H_{24}O_5Si$: C, 55.97; H, 8.05. Found: C, 55.62; H, 7.95.

(±)-Epipentenomycin I (2a). A solution consisting of 81 mg (0.21 mmol) of enone **18a** in 3 mL of acetic acid, 1 mL of H_2O, and 1 mL of THF was stirred at room temperature for 8 days.[44] Removal of solvents in vacuo afforded a yellow oil which was purified via preparative TLC (EtOAc, R_f 0.17) to yield 25 mg (81%) of a colorless oil possessing the following spectral data: IR (neat) 3330 (s, br), 2950 (w), 2910 (w), 1700 (s), 1650 (m), 1125 (m), 1060 (m) cm^{-1}; NMR (Table IV; 60 MHz, D_2O) δ 3.88 (d, J = 2 Hz, 2 H), 5.00 (dd, apparent t, J = 2.0 Hz, 1 H), 6.58 (dd, J = 2.0, 6.5 Hz, 1 H), 7.90 (dd, J = 2.0, 6.5 Hz, 1 H); Chemical ionization mass spectrum: M+1, 145.0497; (Calcd for $C_6H_8O_4$) 145.0500.

(±)-Epipentenomycin III (2c). A solution consisting of 75 mg (0.25 mmol) of enone **18c**,[44] 3 mL of HOAc, 1 mL of H_2O, and 1 mL of THF was stirred at room temperature for 10 days. Removal of the solvents in vacuo afforded 55 mg of an orange oil. Purification via preparative TLC (EtOAc, R_f 0.35) afforded 37 mg (80%) of **2c** as a colorless oil possessing the following spectral data: IR 3500 (m, br), 3000 (m), 2960 (s), 1730 (s), 1725 (s), 1260 (s), 1235 (s), 1000 (s), 950 (s), 820 (m) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 2.06 (s, 3 H), 4.32 (AB q, J_{AB} = 12.0 Hz, 2 H), 4.90 (br s, 1 H), 6.33 (dd, J = 1.7, 6.8 Hz, 1 H), 7.52 (dd, J = 1.7, 6.8 Hz, 1 H); chemical-ionization mass spectrum, m/e 187.0593 (M + 1; calcd for $C_8H_{10}O_5$ 187.0606).

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the National Institutes of Health (National Cancer Institute) through Grant CA-19033. In addition we thank Mr. S. T. Bella of the Rockefeller University for the microanalyses and the Middle Atlantic Regional NMR facility (Grant NIH-RR542) at the University of Pennsylvania where the 220- and 360-MHz NMR spectra were recorded.

Registry No. (±)-**1a**, 68907-79-9; (±)-**1b**, 68907-80-2; (±)-**1c**, 81024-51-3; (±)-**2a**, 77480-52-5; (±)-**2b**, 77480-53-6; (±)-**2c**, 77480-54-7; (±)-**3**, 66655-93-4; **4**, 68882-71-3; **5**, 81024-52-4; (±)-**18a**, 77419-55-7; (±)-**18b**, 77419-59-1; (±)-**18c**, 80963-20-8; (±)-**19a**, 77429-47-1; (±)-**19b**, 80963-21-9; (±)-**19c**, 80963-22-0; (±)-**20a**, 77419-53-5; (±)-**20b**, 77419-57-9; (±)-**20c**, 77419-61-5; (±)-**21a**, 77419-52-4; (±)-**21b**, 77419-56-8; (±)-**21c**, 77419-60-4; (±)-**21d**, 77419-51-3; (±)-**21e**, 80963-23-1; **22a**, 57020-97-0; **22b**, 10481-34-2; **23a**, 80963-24-2; **23b**, 80963-19-5; **29a**, 68241-78-1; **29b**, 70156-97-7; **29c**, 70156-98-8; **31a**, 70156-99-9; **31b**, 1120-73-6; **31b ketal**, 23153-76-6; **31c**, 25564-22-1; **31c ketal**, 80963-25-3; **31d**, 70157-00-5; **31e**, 70157-01-6; **31f**, 60887-85-6; **31g**, 1128-08-1; **31h**, 70157-02-7; **31h** ketal, 80963-26-4; **31i**, 25435-63-6; **31i ketal**, 80963-27-5; **31j**, 80963-28-6; (±)-**32**, 81024-53-5; (±)-**33**, 80963-29-7; **34a**, 68882-72-4; **34b**, 76047-51-3; (±)-**35a**, 68882-73-5; (±)-**36a**, 80963-30-0; (±)-**36b**, 80963-31-1; (±)-**37a**, 80963-32-2; (±)-**37b**, 68882-75-7; (±)-**38**, 80963-33-3; (±)-**39**, 80963-34-4; (±)-**40**, 68882-76-8; (±)-**44**, 68882-74-6; (±)-**45a**, 77419-54-6; (±)-**45b**, 77419-58-0; (±)-**45c**, 80963-35-5; 3-methylcyclopentenone, 2758-18-1; 2-bromo-3-methyl-2-cyclopentenone, 80963-36-6; cyclohexenone, 930-68-7; 2-bromocyclohexenone, 50870-61-6; 2-*n*-butyl-2-cyclohexenone, 34737-39-8.

On the Existence of Stable Structural Isomers of Ketene. A Theoretical Study of the C_2H_2O Potential Energy Surface

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Ab initio molecular orbital theory has been used to study in detail the C_2H_2O potential energy surface. Equilibrium structures and transition structures have been explicitly identified by using gradient techniques and the split-valence 4-31G basis set. Improved relative energies have been obtained by using the split-valence plus dp-polarization 6-31G** basis set with electron correlation incorporated at the levels of second-order (MP2) and third-order (MP3) Møller–Plesset perturbation theory. Zero-point vibrational effects have also been taken into account. Three structures are predicted to be stable, observable species; these are the well-known ketene and the as yet unobserved hydroxyacetylene (ethynol) and oxiranylidene. Of the remaining structures studied, oxirene is found to lie in a shallow potential well with a small barrier to rearrangement to ketene. Two carbenoid species, formylmethylene and hydroxyvinylidene, are predicted to rearrange without activation energy to ketene and hydroxyacetylene, respectively.

Although a considerable number of possible isomeric C_2H_2O structures may be contemplated (Figure 1), only one of these, ketene (1), has been observed experimentally. It is of interest to examine whether any of the other C_2H_2O isomers are likely to be stable observable species, and to this end we have undertaken an ab initio molecular orbital study of the C_2H_2O potential energy surface. The structures examined include ketene (1), hydroxyacetylene

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Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (kJ mol^{-1}) for C_2H_2O Structures

structure	total energy RHF/4-31G	RHF/6-31G**	MP2/6-31G**	MP3/6-31G**	zero-point energy[a]
ketene (1)	−151.494 93	−151.727 87	−152.162 06	−152.167 77	91.3
hydroxyacetylene (2)	−151.444 21	−151.669 53	−152.101 16	−152.110 34	92.8
oxirene (3)	−151.353 97	−151.582 78	−152.031 10	−152.039 79	85.8
formylmethylene (4)	−151.372 60	−151.609 78	−152.018 33	−152.033 61	80.4
hydroxyvinylidene (5)	−151.375 07	−151.605 95	−152.012 66	−152.034 40	87.0[b]
oxiranylidene (6)	−151.369 14	−151.629 33	−152.062 91	−152.074 09	89.5
$^{-}\mathrm{C{\equiv}C{-}}^{+}\mathrm{OH}_2$ (7)	−151.271 80				
CHOCH (8)	−151.286 72				
TS (4 → 1) (10)	−151.366 66	−151.611 98	−152.041 64	−152.049 60	74.7
TS (2 → 4) (11)	−151.293 71	−151.520 59	−151.995 94	−151.986 53	70.6
TS (3 → 4) (12)	−151.343 98	−151.574 07	−152.025 56	−152.025 45	79.6
TS (3 → 5) (13)	−151.270 21	−151.504 43	−151.981 09	−151.978 83	73.5
TS (5 → 2) (14)	−151.347 94	−151.597 53	−152.027 61	−152.040 00	72.9
TS (6 → 4) (15)	−151.263 66	−151.519 92	−151.967 36	−151.974 41	71.1
TS (6 → 2) (16)	−151.239 79	−151.494 32	−151.941 81	−151.947 14	68.3
CH_2 + C≡O	−151.362 70	−151.613 47	−152.006 83	−152.024 15	60.0

[a] Calculated at the RHF/3-21G level, unless otherwise stated. [b] RHF/4-31G value. RHF/3-21G//RHF/4-31G calculations produced one imaginary frequency.

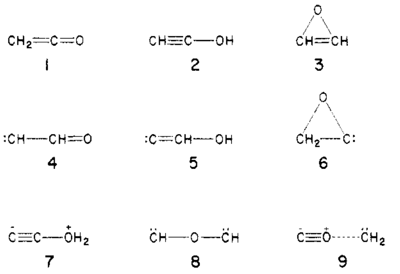

Figure 1. Possible isomeric C_2H_2O structures.

(ethynol 2), oxirene (3), formylmethylene (4), hydroxyvinylidene (5), oxiranylidene (6), and the three somewhat less likely structures 7–9 (Figure 1).

There have been numerous previous theoretical studies of the C_2H_2O system.[1-14] Considerable attention has been focused on ketene (1), oxirene (3), and formylmethylene (4)[2,3,5-8,10,12,13] since they represent prototypes of molecules thought to be involved in the Wolff rearrangement.[14-22] Several studies examine the relative energies of ketene (1), hydroxyacetylene (2), and oxirene (3).[1,9,12,13,15] Oxiranylidene (6), proposed as an intermediate in the photolysis of ketene,[23,24] has also received some attention;[4,7,11] one unsuccessful attempt to generate 6 has been reported.[25] Much of this work has been recently reviewed.[12,14,22,26]

Of the previous theoretical studies, only two[9,13] were performed at a level of theory expected to give quantitatively reliable estimates of relative energies. The study by Tanaka and Yoshimine[13] should be especially noted as a careful and detailed examination of the C_2H_2O surface. However, none of the previous studies determine rigorously the transition structures for interconversion of the isomers, nor has any consideration previously been given to the effects of zero-point vibrations. It was therefore desirable to undertake the present systematic study of the C_2H_2O isomers and their intramolecular rearrangement pathways.

Method and Results

Standard ab initio molecular orbital calculations were carried out by using a modified version[27] of the Gaussian 80 system of programs.[28] Geometries of equilibrium structures and transition structures in the singlet C_2H_2O surface have been determined by using gradient optimization techniques[29] at the restricted Hartree–Fock (RHF) level with the split-valence 4-31G basis set.[30] Improved relative energies have been obtained from higher level calculations which utilize the dp-polarization 6-31G** basis set[31] and which incorporate valence electron correlation

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Table II. Calculated Relative Energies (kJ mol^{-1}) for C_2H_2O Structures

structure	rel energy				
	RHF/4-31G	RHF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP3/6-31G**[a]
ketene (1)	0	0	0	0	0
hydroxyacetylene (2)	133.2	153.2	159.9	150.8	152.1
oxirene (3)	370.1	380.9	343.8	336.0	331.1
formylmethylene (4)	321.2	310.0	377.4	352.2	342.4
hydroxyvinylidene (5)	314.7	320.1	392.2	350.2	346.3
oxiranylidene (6)	330.3	258.7	260.3	246.0	244.3
$^{-}C{\equiv}C{-}{}^{+}OH_2$ (7)	585.8				
CHOCH (8)	546.6				
TS (4 → 1) (10)	336.8	304.3	316.2	310.3	295.3
TS (2 → 4) (11)	528.3	544.2	436.1	475.8	457.2
TS (3 → 4) (12)	396.3	403.8	358.4	373.7	363.1
TS (3 → 5) (13)	590.0	586.6	475.1	496.1	480.0
TS (5 → 2) (14)	385.9	342.2	353.0	335.5	318.9
TS (6 → 4) (15)	607.2	546.0	511.2	507.7	489.5
TS (6 → 2) (16)	669.9	613.2	578.3	579.3	558.6
CH_2 + C≡O	347.2	300.4	407.6	377.1	348.9

[a] Including zero-point energies scaled by 0.9, see: Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem.*, in press.

Table III. Calculated[a] Vibrational Frequencies for C_2H_2O Structures 1–6

compd	frequency, cm^{-1}
ketene (1)	3468 (b_2), 3378 (a_1), 2317 (a_1), 1587 (a_1), 1266 (a_1), 1175 (b_2), 882 (b_1), 663 (b_1), 535 (b_2)
hydroxyacetylene (2)	4043 (a′), 3681 (a′), 2472 (a′), 1290 (a′), 1121 (a′), 947 (a′), 849 (a″), 601 (a″), 516 (a′)
oxirene (3)	3626 (a_1), 3542 (b_2), 1950 (a_1), 1059 (a_1), 1059 (b_2), 903 (a_1), 902 (a_2), 776 (b_1), 524 (b_2)
formylmethylene (4)	3232, 3055, 1793, 1484, 1183, 983, 803, 631, 275
hydroxyvinylidene (5)[b]	3997 (a′), 3352 (a′), 1835 (a′), 1433 (a′), 1223 (a′), 1089 (a′), 891 (a″), 407 (a′), 311 (a″)
oxiranylidene (6)	3470 (a″), 3360 (a′), 1648 (a′), 1415 (a′), 1241 (a′), 1170 (a″), 960 (a″), 903 (a′), 805 (a′)

[a] At the RHF/3-21G level unless otherwise stated. [b] RHF/4-31G//RHF4-31G values: see Table I, footnote *b*.

via second-order (MP2) and third-order (MP3) Møller–Plesset perturbation theory.[32,33] In order to include effects of zero-point vibrations, harmonic frequencies have been determined by using RHF calculations with the 3-21G basis set.[34]

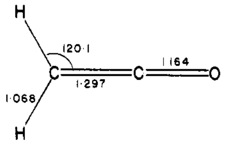
Previous studies[35,36] have concluded that the errors introduced in relative energies by using Hartree–Fock rather than correlated geometries are quite small. In a study[36] of the HNC → HCN and $HOC^+ \rightarrow HCO^+$ rearrangements, it was shown that use of geometries obtained at the RHF/4-31G level rather than those obtained at the MP3/6-31G** level leads to an error of only a few kilojoules per mole in calculated relative energies. We also note that a study[37] of a series of 1,2 hydrogen shifts has shown that MP3 values of isomerization and activation energies are quite close to those obtained from more complete correlation treatments.

Optimized structures (RHF/4-31G) are displayed within the text. Corresponding total energies and zero-point vibrational energies are shown in Table I. Relative energies and vibrational frequencies are given in Tables II and III, respectively.

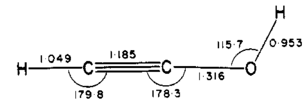
Throughout this paper bond lengths are given in angstroms and bond angles in degrees. Nonindependent parameters are given in parentheses. Unless otherwise noted, all energy comparisons refer to MP3/6-31G** values corrected for zero-point vibrational energy, and relative energies use ketene as the reference point.

Discussion

Structures and Relative Energies. Ketene (1) and hydroxyacetylene (2) have been studied extensively in the past, and their calculated structures warrant no further comment. Hydroxyacetylene is predicted to lie 152 kJ mol^{-1} higher in energy than ketene; previous best estimates[9,13] are 146 and 151 kJ mol^{-1}. This pair of molecules represents the simplest example of ketene–ynol isomerism. It is of interest to note that the ynol–ketene energy difference (152 kJ mol^{-1}) is considerably greater than the enol–keto energy difference (45 kJ mol^{-1})[38] found for the vinyl alcohol/acetaldehyde system.

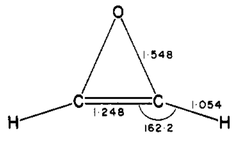


1 (C_{2v})



2 (C_s)

Oxirene (3) has also been the subject of considerable attention. Contrary to earlier reports[3,7] that 3 is nonplanar,



3 (C_{2v})

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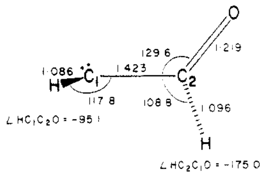
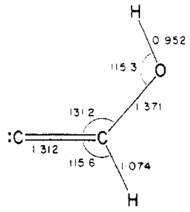
we find no potential energy minimum for a nonplanar structure. The optimized structure (**3**), with C_{2v} symmetry, is found to have an energy 331 kJ mol^{-1} above ketene (**1**); other recent values[9,13] are 335 and 344 kJ mol^{-1}. The high energy of oxirene emphasizes the relative destablizing effect of its 4-π-electron configuration.[39]

The optimized structure of formylmethylene (**4**) has C_1 symmetry. Noteworthy is the orientation of the carbene lone pair which is perpendicular to the formyl group, an orientation stabilized by conjugative interaction with the π^* orbital of the C=O bond. The calculated energy of **4** (342 kJ mol^{-1} above **1**) is slightly higher than a previous best estimate[13] of 331 kJ mol^{-1}.



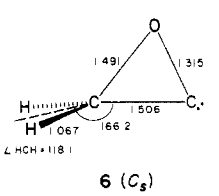
4

No previous studies concerning hydroxyvinylidene (**5**) have been reported. The preferred conformation is found to be planar with the hydroxyl hydrogen syn rather than anti with respect to the (formal) double bond. The energy of **5** (346 kJ mol^{-1} above **1**) is close to that calculated for **4**. Comparing our results for hydroxyacetylene (**2**) and hydroxyvinylidene (**5**) with data obtained[37] for the parent systems acetylene and vinylidene, we find that OH substitution has resulted in small changes in the CC and CH lengths. Thus, CC and CH bond lengths in acetylene are 1.190 and 1.051 vs. 1.185 and 1.049 Å in **2** while CC and CH lengths in vinylidene are 1.296 and 1.074 vs. 1.312 and 1.074 Å in **5**. Electron donation from the p_π lone pair on oxygen into the antibonding π^* orbital of the vinylidene double bond causes a slight elongation of this bond. The energy difference between **2** and **5** of 194 kJ mol^{-1} is slightly higher than the corresponding value calculated for the acetylene/vinylidene system (185 kJ mol^{-1}, MP4/6-311G**//MP2/6-31G* with vibrational corrections).[40]



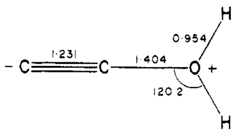
5 (C_s)

Previous studies[4,7,11] of oxiranylidene (**6**) have suggested that it is slightly lower in energy than **3** (by ~45 kJ mol^{-1}). The present results suggest a larger energy difference of 87 kJ mol^{-1}. The energy of **6** (244 kJ mol^{-1} above **1**) makes it the third most stable C_2H_2O isomer after **1** and **2**. This result contrasts with earlier reports[7,11] in which formylmethylene (**4**) was found to be slightly lower in energy (2–7 kJ mol^{-1}) than **6** (cf. our energy difference of 98 kJ mol^{-1} in favor of **6**), the difference arising because of the importance of including polarization functions and electron correlation in describing the relative energies (Table II).



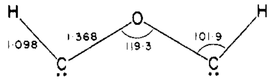
6 (C_s)

Isomer **7** was found to optimize to C_{2v} symmetry, with a structure which might be described as a protonated hydroxyethynyl anion.



7 (C_{2v})

The dicarbene **8** was found to prefer the anti–anti conformation over the syn–anti conformation and has C_{2v} symmetry as shown. This species can be considered to be the C–C ring-opened isomer of oxirene (**3**). Because of the high relative energies at the RHF/4-31G level of **7** and **8** (586 and 547 kJ mol^{-1} above **1**, respectively), they were not examined with higher level calculations.



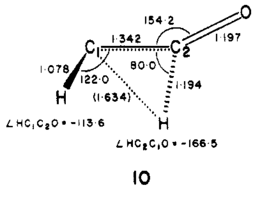
8 (C_{2v})

The last species considered, **9** (Figure 1), resembles a very weak complex of CO and singlet CH_2. However, the higher level calculations indicate that **9** will collapse without activation energy to oxiranylidene (**6**), and it is therefore not considered further in this study.

Intramolecular Rearrangement Pathways. In order to assess the stabilities of the various C_2H_2O isomers with respect to intramolecular rearrangement, it is necessary to determine the potential barriers for such rearrangements as given by the relative energies of appropriate transition structures. Some of the rearrangement pathways have been examined in previous studies.[6,8,11-14] However, in none of these studies were the transition structures rigorously determined, i.e., shown to be stationary points in the potential energy surface for which the force constant matrix has one and only one negative eigenvalue. Transition structures obtained by using a nonrigorous "reaction coordinate" approach clearly are less reliable than those obtained from explicit calculations using gradient techniques.

Our search of the potential energy surface enables us to construct a scheme showing the possible interconversions among structures **1**–**6** (Figure 2).

At the 4-31G level, a transition structure (**10**) was found for the conversion of formylmethylene (**4**) to ketene (**1**). However, the higher level calculations (Tables I and II) indicate that **10** is lower in energy than **4** (by 47 kJ mol^{-1}). This suggests that formylmethylene (**4**) may be able to rearrange without activation to ketene (**1**). A similar conclusion was reached in a "fixed reaction corrdinate" study.[13]



10

Hydroxyacetylene (**2**), only 152 kJ mol^{-1} higher in energy than ketene (**1**), would seem to be a good candidate for experimental observation provided that it is separated from ketene by a sizable potential barrier. In a previous

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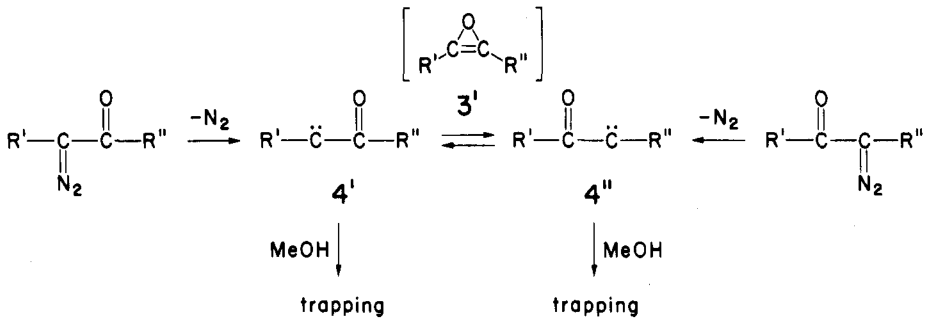
[39] Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.

[40] Krishnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *79*, 408.

Scheme I



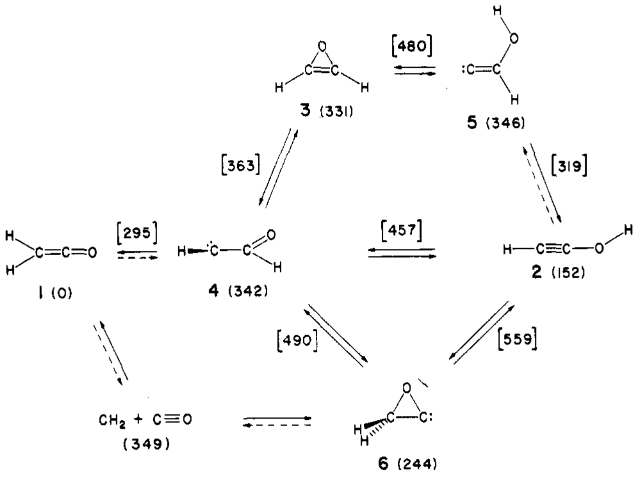
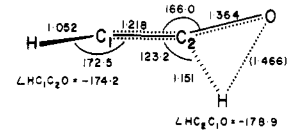


Figure 2. Interconversion pathways between C_2H_2O isomers. Relative energies shown in parentheses are for equilibrium structures; those shown in square brackets are for transition structures.

reaction coordinate study,[13] a barrier of 306 kJ mol^{-1} was reported for this rearrangement; another estimate[9] puts the barrier at ≥85 kJ mol^{-1}. For technical reasons, we were unable to locate a transition structure in the RHF/4-31G surface for the direct 1,3 hydrogen shift from **2** to **1** (see ref 41). We did, however, find a pathway linking **2** and **1** *corresponding to successive 1,2 hydrogen shifts*. In the first step, hydroxyacetylene is converted to formylmethylene via transition structure **11**. The calculated



11

barrier for rearrangement of **2** to **4** is 305 kJ mol^{-1}, which, due to the absence of a barrier for **4** → **1**, becomes the barrier for the hydroxyacetylene/ketene rearrangement via this mechanism. This barrier is large enough to suggest that **2** should be stable with respect to rearrangement via **4** (cf. Figure 3). An approximate transition structure for **2** → **4** has been previously reported[13] with a corresponding barrier of 396 kJ mol^{-1}. It is interesting to note that the barrier to rearrangement in the related vinyl alcohol/acetaldehyde system was found[42] to be 281 kJ mol^{-1}.

The existence of substituted oxirenes has been inferred from labeling studies, notably by Strausz et al., of the Wolff rearrangement,[17-22] and such species have also been suggested as intermediates in the enzymatic oxidation of acetylenes.[43] In agreement with previous studies,[6,13] we find oxirene (**3**) to lie in a potential well on the C_2H_2O surface, and our transition structure (**12**) for the rear-

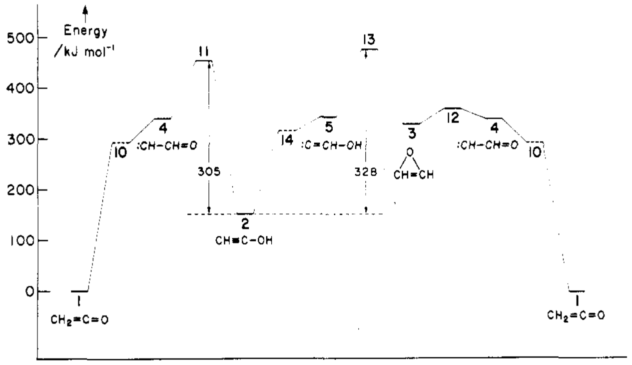


Figure 3. Schematic potential energy profile showing rearrangement pathways from hydroxyacetylene (**2**).

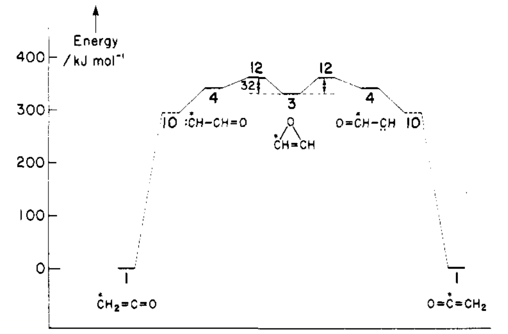
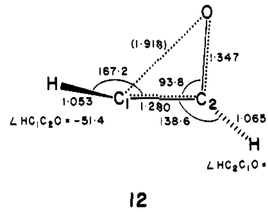


Figure 4. Schematic potential energy profile showing the interconversions which are thought to be involved in the Wolff rearrangement.



12

rangement of **3** to formylmethylene (**4**) confirms results obtained by the reaction coordinate approach.[6,13] Our calculated barrier (32 kJ mol^{-1}) is somewhat higher than the previous best result[13] (8 kJ mol^{-1}) based on an estimated transition structure. In the absence of a barrier for **4** → **1**, the barrier for **3** → **4** also represents the barrier for **3** → **1** (as illustrated in Figure 4). Thus we find that for the prototype Wolff rearrangement where formyl-

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[41] We did locate this saddle point in the RHF/6-31G* surface. Higher level calculations indicate that this direct path may have a barrier ~20 kJ mol^{-1} lower than that for the two-step mechanism **2** → **4** → **1**.

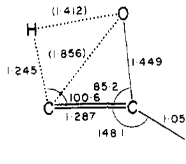
[42] Rodwell, W. R.; Bouma, W. J.; Radom, L. *Int. J. Quantum Chem.* **1980**, *18*, 107.

[43] Ortiz de Montellano, P. R.; Kunze, K. L. *J. Am. Chem. Soc.* **1980**, *102*, 7373.

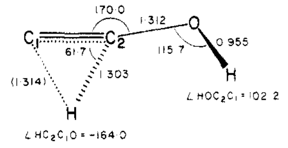
methylene is generated from α-diazoacetaldehyde, the intermediacy of oxirene, which would be necessary to produce scrambling of labeled carbons, requires somewhat more energy than that needed to initially produce formylmethylene. This observation is in agreement with experimental results for α-diazo ketones, where it is found that oxirene participation in the thermal decomposition is temperature dependent.[44,45]

A recent experiment[46] describes the trapping of substituted singlet oxocarbenes (**4′**, **4″**) by reaction with methanol and demonstrates the interconversion shown in Scheme I which presumably involves a substituted oxirene (**3′**). It is of interest to note that thiirene, the sulfur analogue of oxirene, has recently been prepared.[47]

Hydroxyvinylidene (**5**) and oxirene (**3**) have similar energies. A transition structure (**13**) was found linking **5** and **3** via a concomitant 1,2 hydrogen shift and ring-opening by CO bond cleavage. The calculated barrier for **5** → **3** is 134 kJ mol^{-1}. The 4-31G calculations also indicate a transition structure (**14**) for the conversion of **5** to hydroxyacetylene (**2**) via a 1,2 hydrogen shift. However, at the MP3/6-31G** level, **14** becomes lower in energy than **5**, a result reinforced by consideration of zero-point vibrational effects. This suggests that **5** is not a stable isomer; if generated, **5** would be expected to collapse spontaneously to hydroxyacetylene (**2**). This result may be compared with the very small energy barriers (~4 kJ mol^{-1}) calculated[37,40,48] for rearrangement in the unsubstituted vinylidene/acetylene system. Overall, the rearrangement of **5** to **3** via **13** identifies another pathway for the conversion of hydroxyacetylene (**2**) to ketene (**1**) (i.e., **2** → **5** → **3** → **4** → **1**, as shown in Figures 2 and 3), requiring only slightly greater activation energy than the more direct two-step path (**2** → **4** → **1**).

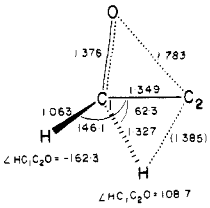


13 (C_s)



14

We have examined several rearrangement pathways to assess the stability of oxiranylidene (**6**). A transition structure (**15**) was found for the 1,2 hydrogen shift converting **6** to **4**; the barrier to this rearrangement is calculated to be large (245 kJ mol^{-1}). A transition structure (**16**) was also obtained for the conversion of **6** to hydroxyacetylene (**2**). This is a 1,2 hydrogen shift with concomitant ring opening via CO bond cleavage, very similar to the process found for **3** → **5** (via transition structure **13**). The barrier for **6** → **2**, however, is calculated to be quite large (314 kJ mol^{-1}). The resulting potential energy profile (Figure 5) implies that **6** should be stable with respect to intramolecular rearrangement to **2** or **1** (via **4**).



15

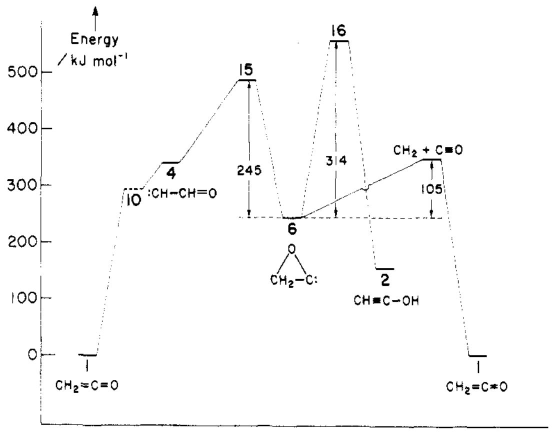
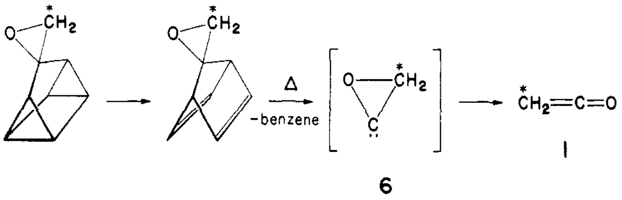
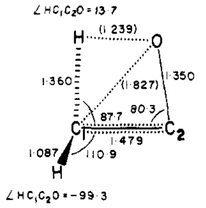


Figure 5. Schematic potential energy profile showing rearrangement pathways from oxiranylidene (**6**).

Scheme II





16

Our attempts to find a transition structure for the direct conversion of **6** to **1** have not been successful. A previously reported estimate[11] of such a transition structure is not supported by our calculations, the gradient norm being large at that point. Ring opening of **6** via O–CH$_2$ bond cleavage is found to lead to dissociation into CH$_2$ (singlet) + CO in a reaction which is endothermic by 105 kJ mol^{-1}. The lowest pathway, therefore, for rearrangement of **6** to **1** would seem to be via the separated species (see Figures 2 and 5) and involves the dissociation energy (105 kJ mol^{-1}) as the barrier. These results are consistent with an experimental attempt[25] at generating **6** (Scheme II). Although ketene (**1**) and not oxiranylidene (**6**) was detected in this experiment, labeling of the CH$_2$ carbon showed that the two carbon atoms had remained distinct, indicating no intermediate presence of the symmetrical oxirene **3**. Our results lead us to suggest that an experiment similar to that of Scheme II, but carried out in the presence of labeled carbon monoxide, might lead to incorporation of the label into the ketene which is formed. It would also seem that the exchange of label in ketene[20,23,24] on photo-

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(44) Matlin, S. A.; Sammes, P. G. *J. Chem. Soc., Chem. Commun.* **1972**, 11.

(45) Matlin, S. A.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2623.

(46) Tomioka, H.; Okuno, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7123.

(47) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1981**, *103*, 486.

(48) Dykstra, C. E.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 1378.

lysis (eq 1), which is likely to proceed via oxirene as an

$$\overset{*}{C}H_2{=}C{=}O \xrightarrow{h\nu} CH_2(\text{singlet}) + \overset{*}{C}O \qquad (1)$$

intermediate, occurs through formylmethylene (**4**) (i.e., **1** $\rightleftarrows$ **4** $\rightleftarrows$ **3**, Figure 4) rather than via a previously suggested[20,23] pathway involving oxiranylidene (**6**) (i.e., **1** $\rightleftarrows$ **6** $\rightleftarrows$ **3** $\rightleftarrows$ **4** $\rightleftarrows$ **1**).

Conclusions

In this paper we have presented the results of a comprehensive study of the C_2H_2O potential energy surface. The following points emerge (cf. Figure 2). (i) The most stable C_2H_2O isomer is ketene (**1**). (ii) Hydroxyacetylene (**2**), lying 152 kJ mol^{-1} higher in energy than ketene but separated from ketene by a barrier of 305 kJ mol^{-1} (via successive 1,2 H shifts), is a potentially observable isomer. (iii) Oxiranylidene (**6**), lying 244 kJ mol^{-1} above ketene (**1**), is also likely to be observable as a stable C_2H_2O isomer, the lowest pathway found for its unimolecular decomposition being dissociation to CH_2 and CO (requiring 105 kJ mol^{-1}). (iv) Two of the possible C_2H_2O isomers, formylmethylene (**4**) and hydroxyvinylidene (**5**), are unstable with respect to intramolecular rearrangement [to ketene (**1**) and hydroxyacetylene (**2**), respectively]. (v) In agreement with previous studies,[6,12–14] we find that oxirene (**3**; 331 kJ mol^{-1} above ketene) lies in a shallow potential well; rearrangement to ketene requires only ~32 kJ mol^{-1} of activation energy and is likely to occur readily under experimental conditions. Consistent with experimental observations, the intermediacy of oxirene in the Wolff rearrangement (as evidenced by scrambling of appropriate labels) is predicted to require energy in excess of the threshold for the reaction.

Acknowledgment. We are indebted to Dr. L. Farnell for the vibrational frequency program. The award of ANU Vacation Scholarship (to C.E.W.) is gratefully acknowledged.

Registry No. 1, 463-51-4; 2, 32038-79-2; 3, 157-18-6; 4, 39920-84-8; 5, 70277-80-4; 6, 50983-85-2; 7, 32038-79-2; 8, 80865-78-7.

Free-Radical Halogenations. 5. Reaction of Chlorosulfonyl Isocyanate with Alkanes[1,2]

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The free-radical chain reactions of chlorosulfonyl isocyanate with alkanes can be initiated with either light or thermal initiators. The major products in these reactions are chlorides, with low yields of isocyanates and sulfonyl chlorides. On the basis of a tertiary to primary hydrogen selectivity of about 120:1 and the relative reactivities of various substrates toward the abstracting radical from chlorosulfonyl isocyanate, the hydrogen-abstracting radical is suggested to be the NCO radical.

Chlorosulfonyl isocyanate (CSI) has been found to be a very reactive isocyanate and to be useful for the preparation of many new and novel compounds through its ionic reactions.[3,4] While considerable attention has been given to the ionic reactions of CSI, the ability of this material to give products arising from free-radical intermediates has not been studied.

Four different hydrogen atom abstracting radicals could be envisioned as arising from CSI. Their hydrogen-abstracting steps are illustrated in Scheme I. The initially formed alkyl radical could then proceed to products by chain transfer with CSI as illustrated in Scheme II. The expected products could then be either isocyanates (via. eq 8 and/or 9), sulfonyl isocyanates (via. eq 10), sulfonyl chlorides (via. eq 5), or chlorides (via. eq 6 and/or 7).

Scheme I

$$RH + Cl\cdot \rightarrow R\cdot + HCl \qquad (1)$$

$$RH + [NCO]\cdot \rightarrow R\cdot + HNCO \qquad (2)$$

$$RH + [SO_2Cl]\cdot \rightarrow R\cdot + SO_2 + HCl \qquad (3)$$

$$RH + [SO_2NCO]\cdot \rightarrow R\cdot + SO_2 + HNCO \qquad (4)$$

Scheme II

$$R\cdot + ClSO_2NCO \rightarrow RSO_2Cl + NCO\cdot \qquad (5)$$

$$\rightarrow RCl + SO_2NCO\cdot \qquad (6)$$

$$\rightarrow RCl + SO_2 + NCO\cdot \qquad (7)$$

$$\rightarrow RNCO + SO_2Cl\cdot \qquad (8)$$

$$\rightarrow RNCO + Cl\cdot + SO_2 \qquad (9)$$

$$\rightarrow RSO_2NCO + Cl\cdot \qquad (10)$$

The actual course of the reaction of the free-radical intermediates from CSI with alkanes could be envisioned as leading to products through synthetically useful and/or mechanistically interesting reactions and has prompted our study.

Discussion of Results

The reaction of cyclohexane with CSI in the presence of benzoyl peroxide afforded 3-substituted cyclohexanes, chlorocyclohexane (93%), cyclohexyl isocyanate (~7%), and cyclohexanesulfonyl chloride (~1%). The chain length for the formation of chlorocyclohexane was found

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[1] A preliminary account of this work was given at the 35th Northwest–5th Biennial Rocky Mountain Joint Regional Meeting Of The American Chemical Society, Salt Lake City, UT, June, 1980; Abstract No. ORGN 22.

[2] Part 4: Mosher, M. W.; Estes, G. W. *J. Am. Chem. Soc.* **1977**, *99*, 6928.

[3] Rasmussen, J. K.; Hassner, A. *Chem. Rev.* **1976**, *76*, 389.

[4] Szabo, W. A. *Aldrichimica Acta* **1977**, *10*, 23.

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