895 cm^{-1}; NMR (250 MHz, CDCl$_3$) δ 0.94 (d, J = 6.6 Hz, 3 H), 1.20–2.25 (comp, 11 H), 2.57 (ddd, J = 2.5, 5.0, 17.5 Hz, 1 H), 2.75 (br d, J = 17.5 Hz, 1 H), 4.88 (m, 2 H); mass spectrum, m/e 190.1362 (M$^+$, calcd for C$_{13}$H$_{18}$O, 190.1357).

(3aS*,4S*,6aR*)-2,4-Dimethyl-1-oxo-3a,6a-propanoperhydropentalene (64). A solution of ketone 63 (300 mg, 1.58 mmol) in ether (15 mL) containing 10% Pt/C (90 mg) was stirred under H$_2$ (1 atm) at room temperature for 1 h. The catalyst was removed by suction filtration and washed with ether (2 × 20 mL). The solvent was distilled off carefully at 1 atm to give 280 mg (92%) of a colorless oil consisting of the two C-8 methyl isomers: IR 2940, 2870, 1670, 900 cm^{-1}; NMR (250 MHz) δ 0.88 (m, 6 H), 1.07–2.30 (comp, 12 H), 2.40 (ddd, J = 2.5, 4.3, 17.8 Hz, 1 H), 2.65 (dd, J = 5, 17.8 Hz, 1 H); mass spectrum, m/e 192.1513 (M$^+$, calcd for C$_{13}$H$_{20}$O, 192.1514).

To a solution of this ketone (280 mg, 1.49 mmol) in benzene (25 mL) was added p-toluenesulfonic acid (369 mg, 1.94 mmol). The mixture was heated to reflux for 18 h and then was allowed to cool to room temperature. The solution was diluted with ether (25 mL), washed with saturated aqueous NaCl (2 × 10 mL), and dried (MgSO$_4$). The solvent was distilled off carefully at 1 atm, and the crude product was purified by preparative HPLC using ethyl acetate/hexane (1:20) as the eluting solvent to give 232 mg (83%) of pure 64 as a colorless oil: IR (CHCl$_3$) 2940, 2860, 1720 cm^{-1}; NMR (250 MHz, CDCl$_3$) δ 0.97 (d, J = 6.6 Hz, 3 H), 1.03 (d, J = 6.7 Hz, 3 H), 1.06–1.93 (comp, 12 H), 2.23 (dd, J = 6.5, 12.8 Hz, 1 H), 2.61 (m, 1 H); mass spectrum, m/e 192.1511 (M$^+$, calcd for C$_{13}$H$_{20}$O, 192.1514).

Anal. Calcd for C$_{13}$H$_{20}$O: C, 81.20; H, 10.48. Found: C, 81.35; H, 10.48.

(3aS*,4S*,6aS*)-3,3a,4,5,6,6a-Hexahydro-1,2,4-trimethyl-3a,6a-propanopentalene (33). To a flask containing methyltriphenylphosphonium bromide (2.31 g, 6.46 mmol) were added tert-amyl oxide (6.48 mmol) and benzene (0.5 mL) at 80 °C under nitrogen. The resulting yellow solution was stirred for 0.5 h at 85 °C, and a solution of ketone 64 (160 mg, 0.83 mmol) in benzene (0.5 mL) was added. The mixture was mixed for another 2 h at 85 °C, and then was allowed to cool to room temperature. The solution was diluted with ether (15 mL), washed with saturated aqueous NaCl (2 × 5 mL), and dried (MgSO$_4$). The solvent was distilled off carefully at 1 atm, and the crude product was purified by flash chromatography using pentane as eluting solvent to give 132 mg (84%) of the desired exocyclic olefin as a colorless oil: IR (CHCl$_3$) 2930, 2850, 1720, 1650, 1435, 880 cm^{-1}; NMR (250 MHz, CDCl$_3$) δ 0.91 (d, J = 6.5 Hz, 3 H), 1.04 (d, J = 6.4 Hz, 3 H), 0.89–1.71 (comp, 12 H), 1.95 (dd, J = 6.4, 12.2 Hz, 1 H), 2.46 (m, 1 H), 4.57 (d, J = 2.5 Hz, 1 H), 4.73 (d, J = 2.5 Hz, 1 H); mass spectrum, m/e 190.1725 (M$^+$, calcd for C$_{14}$H$_{22}$, 190.1722).

To a solution of the olefin (120 mg, 0.63 mmol) in CH$_2$Cl$_2$ (3 mL) was added p-toluenesulfonic acid (50 mg, 0.25 mmol). The mixture was stirred at room temperature for 18 h and then was diluted with CH$_2$Cl$_2$ (10 mL). The resulting solution was washed with saturated aqueous NaCl (1 × 5 mL) and dried (MgSO$_4$), and the solvent was distilled off at 1 atm to give 110 mg (92%) of pure 33 as a colorless oil, identical with the compound obtained previously.

Hexahydro-9,9-dimethyl-1H-3a,8-ethano-5H-dicyclopenta[b,c]furan-5-one (65). To a solution of ether 34 (190 mg, 0.92 mmol) in 10 mL of carbon tetrachloride was added a solution of ruthenium dioxide (12 mg, 0.09 mmol) containing sodium periodate (586 mg, 2.8 mmol) dissolved in 10 mL of water. The reaction was stirred vigorously for 24 h. Carbon tetrachloride was added to the solution, and the layers were separated. Isopropyl alcohol (2 mL) was added to the organics, and the solution was dried over anhydrous potassium carbonate. Removal of the solvent in vacuo gave a dark oil, which was purified via flash chromatography (25% ether, hexane (v/v)) affording 202 mg (100%) of lactone 65: IR (CCl$_4$) 2950 (br s), 2860 (m), 1750 (s), 1450 (w), 1320 (w), 1270 (m), 1190 (m), 970 (m), 910 (s) cm^{-1}; NMR (250 MHz, CDCl$_3$) δ 0.97 (s, 3 H), 1.14 (s, 3 H), 1.17–1.40 (m, 1 H), 1.58–1.96 (m, 10 H), 2.0–2.28 (m, 2 H), 2.56 (br d, J = 11.2 Hz, 1 H); mass spectrum, m/e 220.1464 (M$^+$, calcd for C$_{14}$H$_{20}$O$_2$, 220.1463).

(1R*,3aR*,5aS*,8aS*)-Decahydro-5a-hydroxy-4,4-dimethylcyclopenta[c]pentalene-1-methanol (66). To a stirred solution of lithium aluminum hydride (22 mg, 0.57 mmol) in 20 mL of tetrahydrofuran was added lactone 65 (64 mg, 0.28 mmol), and the solution was warmed to 65 °C for 1 h. The reaction was cooled to room temperature, and solid sodium sulfate decahydrate was added. The salts were removed by filtering them through a pad of Celite and washing with ether. Concentration of the filtrate in vacuo afforded 102 mg of a gummy solid. MPLC (20% ether acetate, hexane (v/v)) gave 57 mg (89%) of 66 as a white crystalline solid: mp 70–72 °C; IR (CHCl$_3$) 3600 (w), 3100–3500 (br m), 2950 (br s), 2860 (m), 1450 (m), 1445 (m), 1375 (w), 1360 (w), 1280 (m), 1260 (m), 1070 (m) cm^{-1}; NMR (250 MHz, CDCl$_3$) δ 1.0 (s, 3 H), 1.08 (s, 3 H), 1.44–2.01 (m, 15 H), 3.14–3.40 (br s, 1 H), 3.84–4.0 (m, 2 H); mass spectrum, 224.1770 (M$^+$, calcd for C$_{14}$H$_{24}$O$_2$, 224.1776).

The Unusual Reactivity of Hydroxymethylene

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Abstract: Hydroxymethylene (1) has been produced by the reaction of arc generated carbon atoms with water, and several of its intermolecular reactions have been studied. Deuterium-labeled 1 reacts with formaldehyde to generate glycolaldehyde (2) which is labeled with deuterium on the aldehydic carbon. This result, along with those obtained from ab initio molecular orbital studies ([MP2/6-31G*]), indicates that 1 reacts with formaldehyde via a 5-center transition state involving nucleophilic attack of the carbene carbon on the aldehydic carbon with concurrent transfer of the hydroxyl hydrogen to the carbonyl oxygen. This mechanism is more favorable than C–H insertion. Studies of the reaction of 1 with 2 and acetaldehyde indicate that the 5-center mechanism predominates in these systems as well. Carbene 1 can also effect intermolecular hydrogenation of an alkene. Thus, generation of 1 in the presence of (Z)-2-butene results in the formation of small amounts of butane. The analogous process in which ethylene is hydrogenated by 1 to form ethane is calculated at the [MP2/6-31G*] level to proceed without barrier.

Hydroxymethylene (1) may be regarded as the parent of a series of carbenes in which the attachment of one or two oxygen atoms to the carbene carbon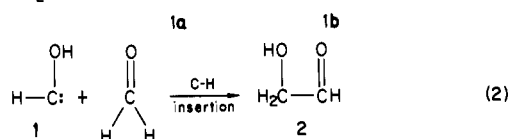 modifies the traditional electrophilicity of the carbene center. The existence of resonance structures such as 1b may bring about ambiphilic or nucleophilic reactivity in such carbenes. Although there have been numerous theoretical studies

Table I. Products and Yields Formed in the Reaction of Arc-Generated Carbon Atoms with Water and/or Formaldehyde[a]

products	C (30.15 mmol) H_2O (222.0 mmol)	C (17.76 mmol) H_2O (222.0 mmol) CH_2O (26.9 mmol)	C (14.4 mmol) D_2O (222.0 mmol) CH_2O (27.8 mmol)
CH_2O	0.976 mmol (3.431 ± 0.201%)		
2	0.273 mmol (0.723 ± 0.157%)	0.199 mmol (1.168 ± 0.093%)	0.213 mmol (1.29 ± 0.165%)
3	7.05×10^{-2} mmol (0.172 ± 0.063%)	6.15×10^{-2} mmol (0.297 ± 0.048%)	5.74×10^{-2} mmol (0.447 ± 0.086%)
4	6.13×10^{-3} mmol (0.015 ± 0.005%)	5.35×10^{-3} mmol (0.026 ± 0.004%)	4.99×10^{-3} mmol (0.039 ± 0.007%)

[a] Molar yields are from typical runs. Percent yields are based on carbon atoms and are the averages of 3 runs with appropriate standard deviations.

of 1,[1-11] there are few experimental reports of its chemistry. Hydroxymethylene has been postulated as an intermediate in the photolysis of formaldehyde (eq 1).[12] When this photolysis is carried out in a low-temperature matrix, one of the products is glycolaldehyde (2), which is postulated to arise from the reaction of 1 with an additional molecule of formaldehyde. It is tempting

$$CH_2=O \xrightarrow{h\nu} H\overset{\cdot\cdot}{\underset{}{C}}-OH \longleftrightarrow H-\overset{-}{C}=\overset{+}{O}H \qquad (1)$$

$$\begin{array}{cc} \textbf{1a} & \textbf{1b} \end{array}$$

$$(2)$$

to postulate that this reaction occurs via insertion into the C–H bond of formaldehyde as shown in eq 2, a reaction which is observed for methylene.[13] However, Kemper, Hoeks, and Buck[1] have carried out a theoretical study of this reaction in which they reach the interesting conclusion that the most likely route to 2 is via the 5-center concerted reaction in eq 3. To date, there have

$$(3)$$
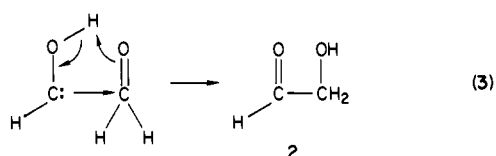
been no experimental attempts to elucidate the mechanism of the reaction of 1 with formaldehyde. Carbene 1 is also unique in that it has the potential for acting as a hydrogen donor in the presence of a suitable acceptor. In fact, Kemper, Hoeks, and Buck[1] have calculated that hydrogenation of formaldehyde by cis-1 (eq 4) is a facile process. The driving force for this unique hydrogenation, which is reminiscent of reductions by diimide, is undoubtedly the

concurrent formation of the rather stable carbon monoxide molecule.

$$(4)$$
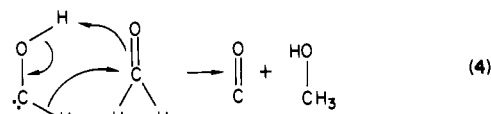
We recently reported an experimental and theoretical study of the reaction of atomic carbon with water in which we concluded that the reaction proceeds via the intermediacy of 1 as shown in eq 5.[11] Since our calculations and previous theoretical work[7]

$$(5)$$
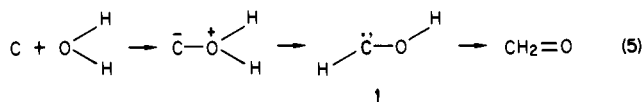
indicate that there is a substantial barrier to the rearrangement of 1 to formaldehyde (∼39 kcal/mol), the carbon–water reaction may represent a system in which 1 may be trapped and its intermolecular reactions studied. In this paper, we report an investigation of the intermolecular chemistry of 1 in which we elucidate the mechanism of the formation of 2 through the use of deuterium labeling, study the reaction of 1 with several higher aldehydes, and evaluate the potential of 1 as a hydrogen donor. Concurrent with these experimental investigations, we have calculated the energetics of a number of the intermolecular reactions of 1.

The Mechanism of the Reaction of Hydroxymethylene with Formaldehyde. In these investigations, we have used the reaction of atomic carbon with water (eq 5) to generate 1. This reaction is analogous to an earlier report of Skell and Harris,[14] who found that arc-generated carbon atoms react with alcohols at 77 K by both O–H and C–H insertion (eq 6). The fact that reactions

$$R-OH + C \rightarrow R-O-\overset{\cdot\cdot}{C}-H + \text{C–H insertion products} \qquad (6)$$
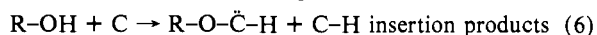
of arc-generated carbon are carried out at low temperature can be used to advantage in the current study to slow the intramolecular rearrangement of 1 to formaldehyde and allow competing intermolecular reactions to occur. When arc-generated carbon atoms were condensed with water at 77 K, formaldehyde was the major product. Interestingly glycolaldehyde (2) along with smaller amounts of glyceraldehyde (3) and dihydroxyacetone (4) were also produced in the carbon + water reaction (eq 7). Since 2,

$$(7)$$
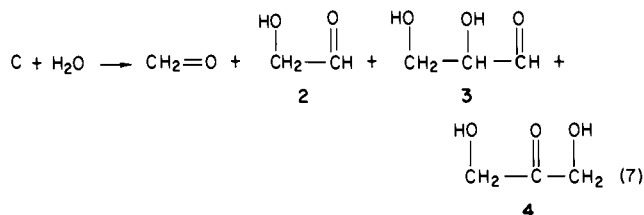
3, and 4 are carbohydrates, we found it convenient to identify and quantitate them by preparing oxime–Me₄Si derivatives[15,16] which

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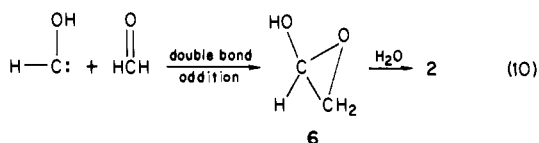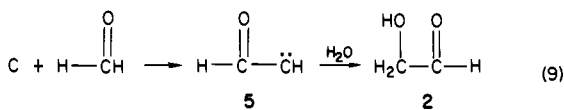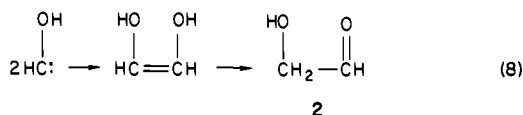(13) Back, M. H. *Can. J. Chem.* **1965**, *43*, 106.

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Table II. Energies Calculated for Intermolecular Reactions of *cis*- and *trans*-Hydroxymethylene (1)[a]

molecular species	3-21G	6-31G	MP2/6-31G	6-31G*	6-31G[c]	ZPE[d]	[MP2/6-31G*][b,c]
CH$_2$O + *trans*-1	226.36811	227.53679	227.94938	227.64678	0	35.60	0
complex	226.38498	227.54930	227.96612	227.65762	-7.8	38.10	-7.0
2	226.48442	227.65532	228.07915	227.76032	-74.4	41.09	-72.8
6	226.44557	227.61089	228.03748	227.72256	-46.5	41.19	-49.8
7	226.38352	227.54402	227.96917	227.65206	-4.5	38.75 (279i)	-8.0
8	226.33671	227.51977	227.93868	227.62815	10.7	37.58 (239i)	9.7
9	226.35864	227.52414	227.95411	227.63256	7.9	39.02 (499i)	1.4
C$_2$H$_4$ + *cis*-1	190.73724	191.72150	192.09585	191.80424	0	51.52	0
12	190.71014	191.68272	192.10149	191.76636	24.3	51.02 (1927i)	-4.6
C$_2$H$_6$ + CO	190.88725	191.86418	192.26465	191.96390	-89.5	53.36	-114.7

[a] Energies in the first four columns are in hartrees while those in the last three columns are in kcal/mol.   [b] Including zero-point correction.   [c] Energies are relative to CH$_2$O + *trans*-1 for the C$_2$O$_2$H$_4$ surface and relative to C$_2$H$_4$ + *cis*-1 for the C$_3$OH$_6$ surface.   [d] Values in parentheses are the calculated imaginary frequencies for the transition state in cm^{-1}.

were analysed by gas chromatography–mass spectrometry (GC–MS). Products and yields in this reaction are given in Table I. The fact that formaldehyde is generated in this reaction is good evidence for the intermediacy of **1**. We shall now turn our attention to the question of the mechanism of the formation of **2**.

In addition to the direct C–H insertion (eq 2) and the 5-center mechanism (eq 3), there are at least three other possible pathways to **2** in the carbon + water reaction. Dimerization of **1** would give 1,2-ethanediol which would tautomerize to **2** as shown in eq 8. An insertion by carbon into the C–H bond of formaldehyde would give formylmethylene (**5**), which could subsequently insert into an O–H bond of water to generate **2** (eq 9). Finally, addition of **1** to the carbon–oxygen double bond of formaldehyde would produce hydroxyoxirane (**6**), which would undoubtedly react with water under the reaction conditions to yield **2** (eq 10).

$$2HC: \longrightarrow HC=CH \longrightarrow CH_2-CH \qquad (8)$$

2

$$C + H-CH \longrightarrow H-C-CH \xrightarrow{H_2O} H_2C-C-H \qquad (9)$$

5   **2**

$$H-C: + HCH \xrightarrow[\text{addition}]{\text{double bond}} C \xrightarrow{H_2O} 2 \qquad (10)$$

6

In order to evaluate the various mechanisms for the formation of **2**, carbon atoms were reacted with D$_2$O in the presence of protiated formaldehyde. This reaction should generate deuterated **1** and an analysis of the deuterium distribution in **2** should allow us to rule out some of the possible mechanisms for the formation of **2**. For example, **2** generated by the dimerization of **1** should have a deuterium on the aldehydic and two deuteriums on the methylene carbons. If **2** is produced by C–H insertion (eq 2) or via formylmethylene (eq 9), it will contain one deuterium on the methylene carbon. Alternately, **2** generated either by the 5-center mechanism (eq 3) or through the intermediacy of **6** (eq 10) will have deuterium on the aldehydic carbon.

When the reaction of carbon with D$_2$O + CH$_2$=O was carried out, the mass spectrum of the oxime–Me$_4$Si derivative of **2** indicated that this molecule contained one deuterium and that this deuterium was on the aldehydic carbon. The mass spectrographic analysis involved the fragmentations shown in eq 11 in which the observation of a *m/e* 205 peak demonstrates that the molecule contains 1 deuterium while the *m/e* 103 peak shows that this deuterium is not on the saturated carbon. In order to ensure that

these conclusions are correct, the reaction of C with D$_2$O alone was run. In this case, the mass spectrum contained peaks at *m/e* 207 and 105, indicating that three deuteriums were present in the oxime–Me$_4$Si derivative of **2** and that two of these deuteriums are on the methylene carbon. These fragmentations are consistent with those previously reported for oxime–Me$_4$Si derivatives of sugars.[17]

$$\text{(structures, eq 11)} \qquad (11)$$

m/e 219   *m/e* 204

m/e 103
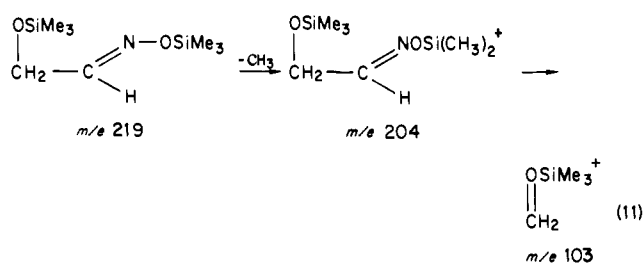
These deuterium-labeling experiments serve to rule out the mechanisms in eq 2, 8, and 9 for the formation of **2**. It is not surprising that the mechanisms in eq 8 and 9 are not operative. It is unlikely that **1** would live long enough for the dimerization in eq 8 to take place. Since we have previously shown that carbon atoms react with formaldehyde by deoxygenation to give methylene,[18] the reaction of carbon with formaldehyde to generate formylmethylene (**5**) (eq 9) in these reactions is unlikely. If **5** were an intermediate, it would probably undergo a Wolff rearrangement to generate ketene rather than react intermolecularly with water. The fact that **2** is not formed by the C–H insertion in eq 2 is consistent with the calculations of Kemper, Hoeks, and Buck[1] in which, although an activation enthalpy is not reported, C–H insertion is found to be a high-energy process.

Theoretical Evaluation of the Reaction between 1 and Formaldehyde. In order to distinguish between the 5-center transition state in eq 3 and the addition to the double bond in eq 10 for the formation of **2** and to evaluate the energetics of direct C–H insertion, we have carried out ab initio calculations of these three intermolecular reactions of **1**. In these calculations, all stationary points have been located by using the GAUSSIAN 82[19] program package with no constraints except for symmetry when appropriate. The 3-21G basis set has been used to determine geometries. The geometries have been optimized by using analytical deriva-

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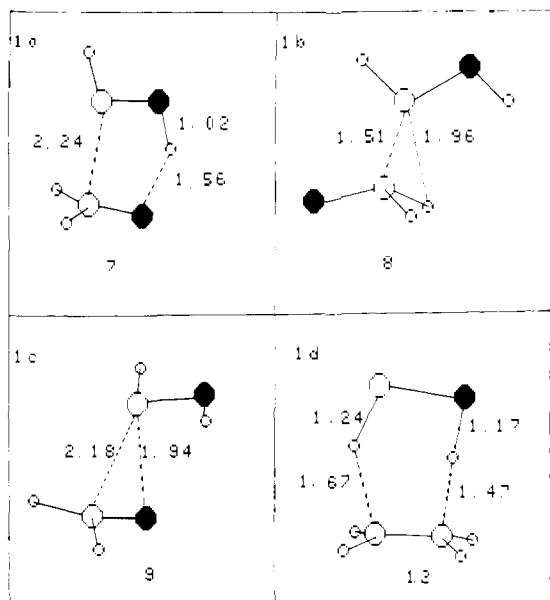
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Figure 1. 3-21G geometries of stationary points for various intermolecular reactions of hydroxymethylene with formaldehyde (a–c) and with ethylene (d). Filled balls represent oxygen atoms.

tives, and transition states have been located by finding a stationary point that has a developing negative eigenvalue in the updated matrix of second derivatives during optimization.[20] The relative energies of the geometry-optimized species were calculated at the [MP2/6-31G*] level.[21] Force constant calculations have been performed in order to estimate zero-point corrections at the 3-21G level as well as to confirm the identification of transition states.

Table II lists the energetics of the various stationary points that were determined in this investigation. The Cartesian coordinates of all species in Table II have been deposited as Supplementary Material. It is interesting that, at the 3-21G level, a stable complex between *trans*-1 and CH_2=O as well as a transition state for the 5-center reaction is found. However, at the [MP2/6-31G*] level, the complex is found to be less stable than the transition state for the 5-center reaction. Thus, it is likely that the addition of *trans*-1 to formaldehyde via the 5-center mechanism in eq 3 proceeds without barrier. The geometry of the transition state 7 calculated for this reaction at the 3-21G level is shown in Figure 1a. Houk, Rondan, and Mareda[22] have recently found computationally that reactive halocarbenes, at the 3-21G level, form intermediate complexes in their cycloaddition reactions. However, in analogy with our results, these energy minima disappear at higher levels of computation.

The determination of the energy of the transition state for the C–H insertion of 1 on formaldehyde proved to be a very difficult task. The search for a stationary point was made exceedingly complicated by the fact that in nearly all geometries there was a strong tendency to transfer the hydroxyl hydrogen on 1 to the carbonyl oxygen of formaldehyde. This difficulty was finally surmounted and a transition state was located in which the carbonyl oxygen and the hydroxyl are anti to one another. The geometry of this transition state 8, which is calculated to have a barrier of 16.7 kcal/mol with respect to the complex, is shown in Figure 1b. The transition state 9 for addition of 1 to the double bond of formaldehyde to generate 6 is shown in Figure 1c. This process is calculated to have an activation energy of 8.4 kcal/mol.

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(21) (a) We have approximated full MP2/6-31G* calculations by combining separate 6-31G* and MP2 calculations. Additivity has been demonstrated to be accurate to within 1–4 kcal/mol of the full calculation.[21b,c] We suggest that calculations which use additivity enclose the appropriate basis set in brackets. (b) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673. (c) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497.

(22) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291.

The results of these calculations, which are in qualitative agreement with those of Kemper, Hoeks, and Buck,[1] indicate that the most favorable mode of reaction of 1 with formaldehyde generates 2 via the 5-center mechanism in eq 3. Although our deuterium-labeling study cannot rule out a mechanism involving oxirane (6), the calculations clearly demonstrate that this is a less favorable pathway and would not be expected to occur. This result parallels the work of Rondan, Houk, and Moss,[23] who calculated the reaction coordinates for the addition of a series of carbenes to ethylene and found that as the stability of the carbene increases there is a corresponding increase in the barrier to cycloaddition. In the present case, it is expected that the adjacent electron pair on oxygen will lead to stabilization of 1 relative to a carbene such as methylene. This effect combined with the increased strain energy in the product appears to preclude formation of 6.

The most striking aspect of both the experimental and theoretical results is the observation of the 5-center reaction in eq 3. This reaction, which is without precedent in carbene chemistry, appears to be brought about by a combination of the increased nucleophilicity of the carbene and the strong tendency for donation of the hydroxyl proton. Both of these effects result from the contribution of resonance structure 1b in which the charge separation favors the reaction in eq 3.

The Reaction of 1 with Higher Aldehydes. The fact that glyceraldehyde (3) is observed in this reaction is evidence that the 5-center addition of 1 to carbonyl compounds occurs in the reaction of 1 with 2 as shown in eq 12. In this case the insertion of 1 into the aldehydic C–H bond appears to be competative and results in dihydroxyacetone (4) (eq 13). The ratio of glyceraldehyde to dihydroxyacetone of 11.5:1 indicates that 5-center addition predominates in this system.


$$(12)$$

$$(13)$$
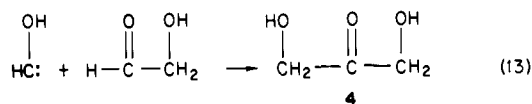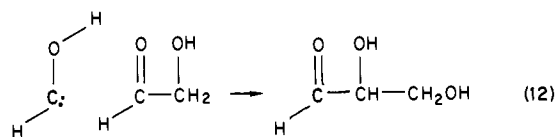
In order to explore the scope of this unusual reaction, we have examined the reaction of 1 with acetaldehyde by reacting C + H_2O in the presence of acetaldehyde. This system generates lactaldehyde (10), a product of 5-center addition, and hydroxyacetone (11), resulting from aldehydic C–H insertion, in a 2.7:1 ratio. It is interesting that no 3-hydroxypropanal, the product of methyl C–H insertion, is observed. A similar preference for aldehydic C–H insertion over methyl C–H insertion is observed in the reaction of methylene with acetaldehyde.[13]


$$10$$
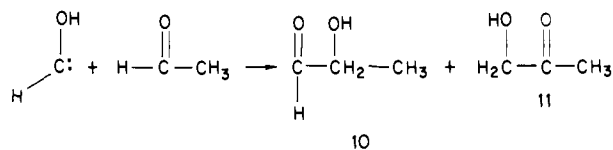
Thus, in the reaction of 1 with both 2 and acetaldehyde, the 5-center addition predominates. However, unlike the reaction of 1 with formaldehyde, some insertion into the aldehydic C–H bond is observed in these cases. It may be that the diminished steric accessability of the carbonyl carbon in 2 and acetaldehyde as compared with formaldehyde decreases the probability of nucleophilic attack by the carbene carbon and allows aldehydic C–H insertion to compete.

Hydroxymethylene as a Hydrogen Donor. Kemper, Hoeks, and Buck[1] have calculated that the donation of two hydrogens from *cis*-1 to formaldehyde to form methanol (eq 4) is a facile process. This mechanism was invoked to explain the formation of methanol in the low temperature matrix photolysis of formaldehyde.[12] Thus, the mechanism in eq 4 predicts methanol as a product of the C

+ H_2O + CH_2=O reaction. Although we do observe methanol in this system, its presence cannot be regarded as confirmatory of the mechanism in eq 4. An alternative route to methanol is deoxygenation of formaldehyde to CH_2[18] which reacts with water to give methanol (eq 14).[24]

$$CH_2\text{=O} + C \rightarrow CO + :CH_2 \xrightarrow{\ H_2O\ } CH_3OH \qquad (14)$$
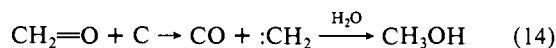
In order to evaluate hydroxymethylene as a hydrogen donor, we have carried out the carbon + water reaction in the presence of (Z)-2-butene as a hydrogen acceptor. As shown in eq 15, this reaction does produce *n*-butane although in very low yield (0.017% based on carbon). The mixture of products from this reaction

$$C + H_2O + \ \backslash\_\_/ \ \rightarrow CO + \ \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown \qquad (15)$$
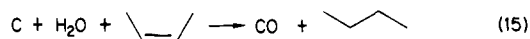
is quite complex and, in this preliminary study, no attempt was made to identify any product other than butane which was analyzed by GC–MS. Reaction of C + D_2O + (Z)-2-butene gave a product whose mass spectrum indicated it to be butane-*2,3-d₂*.

As a model for the reaction in eq 15, we have calculated the activation enthalpy for the transfer of hydrogen from *cis*-1 to ethylene using the computational methods discussed above. The results of these calculations are similar to those for the process in eq 3 in that a transition state is found at the 3-21G level for this reaction, **12**, shown in Figure 1d. However, this transition state disappears at the [MP2/6-31G*] level of calculation and thus the transfer of hydrogen from *cis*-1 to ethylene proceeds without barrier. It should be pointed out that, while *cis*-1 is required for the hydrogen transfer reaction, the reaction between carbon and water in eq 5 will initially generate *trans*-1. The calculated barrier to trans–cis isomerization of 27 kcal/mol[7] indicates that this reaction will be slow at 77 K. However the production of *trans*-1 in the C + H_2O reaction is exothermic by some 115 kcal/mol,[25] and this excess energy may bring about some trans–cis isomerization before it is dissipated in the matrix. Nevertheless, it may be the fact that **1** is predominantly in the trans form that accounts for the low yields in the hydrogenation of (Z)-2-butene.

Summary

The experiments and theoretical calculations reported herein identify a new type of carbene reactivity, involving the transfer of a hydrogen β to a carbene center concurrent with nucleophilic addition of the carbene carbon. Hydroxymethylene, with its adjacent electron pair and labile hydroxyl hydrogen, is ideally suited to exhibit such reactivity. The results further indicate that a second unique mode of reaction of hydroxymethylene is intermolecular hydrogenation of an appropriate acceptor. It remains to be seen if this reactivity pattern will be general for other carbenes, such as mercaptomethylene and aminomethylenes which have electronic structures similar to that of hydroxymethylene.

Experimental Section

Reaction of Arc-Generated Carbon Atoms with Water. An apparatus similar to that described by Skell and co-workers was used to generate carbon atoms. An intermittent arc was struck by passing the current of 48 A between two graphite electrodes. In a typical experiment, water (222.0 mmol) was introduced as a vapor and deposited on liquid N_2 cooled walls where it reacted with carbon (30.2 mmol). At the conclusion

of the reaction, volatile products were pumped through traps at 77 and 195 K. The contents of the 77 K trap were analyzed by IR spectroscopy and found to contain 0.98 mmol of formaldehyde. The nonvolatile products remaining in the reactor bottom were collected by rinsing the reactor with distilled water and filtering the resulting solution. The filtrate and the contents of the 195 K trap were combined and converted to oxime derivatives by the addition of hydroxylamine hydrochloride (160 mg, 2.3 mmol). The water was removed from the mixture of oximes which were converted to Me_4Si derivatives by standard procedures. The Me_4Si–oxime derivatives were analysed by GC and GC–MS on a 6 ft 5% SE-30 column. In all cases, retention times and mass spectra were identical with those of authentic samples. The analysis revealed the presence of glycolaldehyde (**2**) (0.27 mmol) and a mixture of glyceraldehyde (**3**) and dihydroxyacetone (**4**) (7.7 × 10^{-2} mmol) which were not separated as Me_4Si–oxime derivatives under the GC conditions. Mass spectrum of **2**–oxime–Me_4Si (EI): *m/e* (rel intensity) 204 (17.1), 190 (1.5), 147 (100), 130 (16.7), 103 (6.5).

In order to determine the ratio of **3** to **4**, the products of another reaction were converted to simple Me_4Si derivatives and analyzed by GC and GC–MS. Although the Me_4Si derivatives of **3** and **4** are incompletely separated by GC, their mass spectra are different. Mass spectrum of **3**–Me_4Si: *m/e* (rel intensity) 263 (100), 233 (54.3), 205 (6.2), 103 (89.4), 73 (76.0). Mass spectrum of **4**–Me_4Si: *m/e* (rel intensity) 366 (100), 275 (43), 203 (2.4), 103 (28), 73 (80.3). Comparing the ratio of intensity of *m/e* 263 and 366 in a standard mixture of the Me_4Si derivatives of **3** and **4** to that of the reaction product gave the ratio of **3** to **4** as 11.5:1.

Reaction of Arc-Generated Carbon Atoms with D_2O in the Presence of Formaldehyde. Formaldehyde was prepared by the pyrolysis of paraformaldehyde and distilled from 195 to 77 K. In a typical reaction, formaldehyde (27.6 mmol) and D_2O (222 mmol) were introduced separately into the reactor and condensed at 77 K with carbon (14.4 mmol). Glycolaldehyde (0.213 mmol), glyceraldehyde, and dihydroxyacetone (6.2 × 10^{-2} mmol) were analyzed as silylated oxime derivatives. Mass spectrum of the glycolaldehyde–oxime–Me_4Si: *m/e* (rel intensity) 205 (6.6), 204 (1.3), 191 (0.7), 147 (100), 131 (7.7), 130 (1.04), 103 (3.4). These data indicate that the glycolaldehyde contained 1 deuterium on the aldehydic carbon.

Reaction of Arc-Generated Carbon Atoms with Water in the Presence of Acetaldehyde. Water (222 mmol) and acetaldehyde (44 mmol) were introduced separately and condensed with carbon (25.9 mmol) at 77 K. After the reaction, volatile products were passed through traps at 209 and 77 K and the reactor bottom rinsed with water. The rinsings and the contents of the 209 K trap were combined and converted to silylated oxime derivatives. Analysis by GC–MS showed 0.180 mmol of **10**. Although lactaldehyde (**10**) and hydroxyacetone (**11**) are separated as silylated oxime derivative by GC, the derivative of **11** was not separated from silylated hydroxylamine. However, the ratio of these compounds could be determined from their mass spectra, and a yield of **11** of 0.078 mmol was determined. No 3-hydroxypropanal was detected.

Reaction of Arc-Generated Carbon Atoms with Water in the Presence of (Z)-2-Butene. Water (222 mmol) and (Z)-2-butene (11.1 mmol) were introduced separately into the reactor and condensed with carbon (55.9 mmol) at 77 K. After the reaction, volatile products were passed through the traps at 195, 142, and 77 K. The contents of the 142 K trap were analyzed for *n*-butane (7.1 × 10^{-3} mmol) by GC–MS.

(23) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.
(24) Hatakeyama, S.; Bandow, H.; Okuda, M.; Akimoto, H. *J. Phys. Chem.* **1981**, *85*, 2249.
(25) The heat of formation of **1** has been reported to be 26.5 kcal/mol: Pau, C.-F.; Hehre, W. *J. Phys. Chem.* **1982**, *86*, 1252.