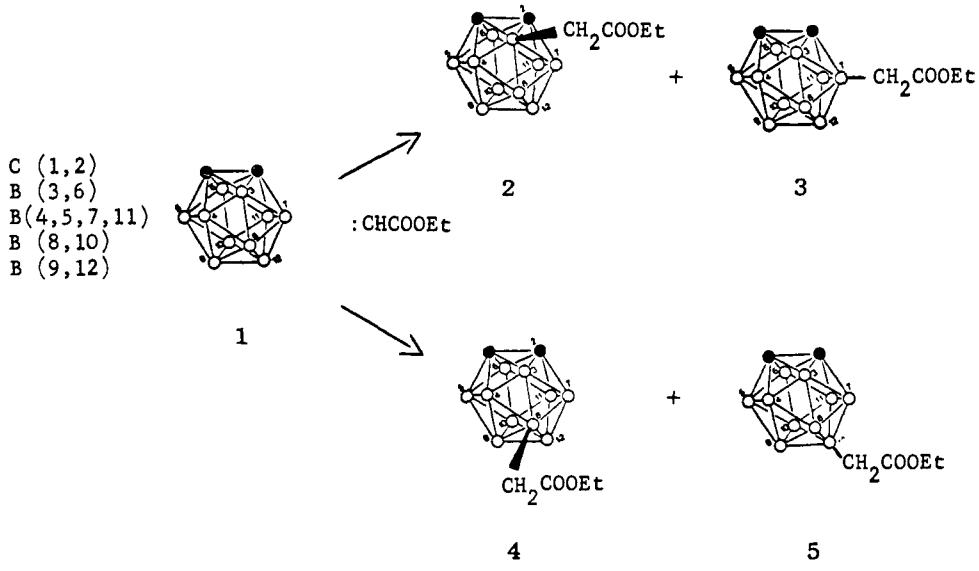
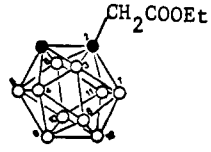
Scheme I




are the four possible products of insertion into the boron–hydrogen bonds of **1**. The carbene ignores the available C–H bond. We have independently synthesized **6**[16] and are unable to detect it in the crude reaction mixture.




6

Carboranes incorporating six-membered rings are unknown.[10] In our case formation of a carborane version of cycloheptatriene would not only expand one five-membered ring of the polyhedron but interrupt conjugation as well. So we are not surprised that insertion products appear instead. Electrophilic substitution in **1** favors the most electron-rich bonds. Friedel–Crafts halogenation proceeds first at the 9,12-position, followed by the 8,10-position.[11a] The other sites are not attacked. Carbethoxycarbene, a known electrophile, behaves similarly. The C–H bonds are not attacked, and the products are formed roughly in proportion to the calculated framework charges in **1**, although the 9,12-position seems to be especially favored, as predicted by Lipscomb et al.[17]

Allylic or benzylic carbon–hydrogen bonds are known to be expecially active in carbon–hydrogen insertion.[18] Doubtless the transition state for insertion benefits in energy terms from conjugation between the breaking carbon–hydrogen bond and the orbitals of the ring. No such benefit accrues to 1-methyl-*o*-carborane. Although our analysis of this system is not yet complete, it is clear that boron–hydrogen insertion is still strongly favored. This is not surprising as the carborane framework, aromatic though it be, is known to be connected only inefficiently to an external free valence.[19]

Regiospecific substitution at boron is notoriously difficult, especially at the 3,6- and 4,5,7,11-positions. Carbene reactions provide a new route to such B-substituted carboranes. We will report later on other carbenes,[20] the effect of spin state, and the possible intervention of 13-vertex carboranes in this apparently simple reaction.

**Registry No.** 1, 16872-09-6; **2**, 86748-07-4; **3**, 86748-08-5; **4**, 86765-91-5; **5**, 86765-92-6; :CHCOOEt, 3315-61-5; ethyl diazoacetate, 623-73-4.

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(17) Dixon, D. A.; Keier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226.
(18) Reference 5, pp 229 ff.
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## Possible Involvement of Excited Singlet Methylene in the Deoxygenation of Formaldehyde by Atomic Carbon

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Although a great deal is known about the chemistry of singlet ($^1A_1$) and triplet ($^3B_1$) methylene,[1] there have been few studies of the first excited singlet state ($^1B_1$). Hoffmann[2] has reported a theoretical investigation that makes the interesting prediction that the addition of $CH_2(^1B_1)$ to alkenes should be nonstereospecific. Experimental studies of the short-wavelength photolysis of ketene, in which $CH_2(^1B_1)$ is postulated, support this prediction.[3,4] We now report experimental results that are consistent with the formation $CH_2(^1B_1)$ in the carbon atom deoxygenation of formaldehyde (eq 1) and which indicate that this species adds in a stepwise manner to alkenes.

$$CH_2{=}O + C \rightarrow CO + CH_2 \qquad (1)$$

In this study, we have generated atomic carbon by the thermolysis of 5-diazotetrazole[5] in the presence of gaseous formaldehyde and have taken advantage of the well-documented[6]

(1) For reviews of experimental and theoretical work on $CH_2$ see: (a) Harrison, J. F. *Acc. Chem. Res.* **1974**, 7, 378–384. (b) Gaspar, P. P.; Hammond, G. S. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. II, pp 207–362. (c) Borden, W. T.; Davidson, E. R. *Annu. Rev. Phys. Chem.* **1979**, *30*, 125–153.
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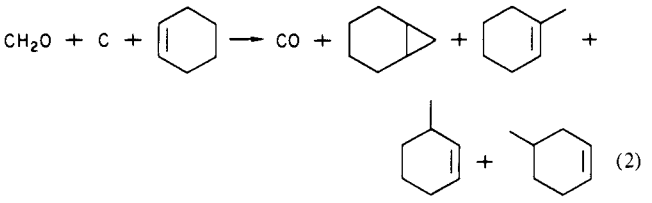
Table I. Cyclopropane Yields and Stereochemistries in the Reaction of $CH_2$ with 1

| reactants[a] (torr) | total yield of dimethylcyclopropanes: [CDC] + [TDC]- ($\times 10^4$ mmol) | total yield of dimethylcyclopropanes: % (CDC + TDC)[b] based on CO | CDC/TDC |
|---|---|---|---|
| 1. $CH_2O$ (7.8), *c*-C–C=C–C (7.1) | 8.15 ± 1.08 | 3.45 ± 0.50 | 1.12 ± 0.23 |
| 2. $CH_2O$ (7.1), *c*-C–C=C–C (7.1), $O_2$ (1.6) | 8.41 ± 1.43 | *d* | 1.17 ± 0.16 |
| 3. $CH_2O$ (7.1), *c*-C–C=C–C (7.1), $N_2$ (200) | 11.65 ± 3.7 | *e* | 2.4 ± 0.6 |
| 4. $CH_2O$ (17.1), *c*-C–C=C–C (200) | 4.42 ± 1.08 | 3.10 ± 1.4 | 1.07 ± 0.28 |
| 5. $CH_2O$ (17.2), *c*-C–C=C–C (620) | 1.09 ± 0.29 | 5.09 ± 1.5 | 1.00 ± 0.19 |
| 6. $CH_2N_2$ (4.0), *c*-C–C=C–C (27)[c] | | | 1.85 |
| 7. $CH_2N_2$ (0.5), *c*-C–C=C–C (1.9), $N_2$ (201)[c] | | | 2.79 |
| 8. $CH_2N_2$ (0.9), *c*-C–C=C–C (231)[c] | | | 5.27 |

[a] In all deoxygenations, C atoms were generated by the thermolysis of 1.38 mmol 5-diazotetrazole. [b] Yields based on CO generated. [c] Reference 12. [d] Since CO is generated by reaction of $C(^3P)$ with $O_2$, CDC + TDC based on CO could not be calculated. [e] CO cannot be analyzed by GC in the presence of the large excess of $N_2$.

deoxygenation reaction.[7] Deoxygenation of $CH_2O$ by $C(^1D_1)$ to generate $CH_2(^3B_1)$, $CH_2(^1A_1)$, and $CH_2(^1B_1)$ is exothermic by 106.8, 92.8 ± 6, and 71.7 ± 6 kcal/mol,[8] respectively, indicating ample energy for the production of all three electronic states of $CH_2$.

That this reaction does produce methylene is indicated by the fact that thermolysis of 5-diazotetrazole in an atmosphere of formaldehyde and cyclohexene generates the products in eq 2.



(2)

Products of methylene addition to cyclohexene total 10% based on carbon monoxide production.

In order to assess the stereochemistry of the $CH_2$ addition, we have carried out the deoxygenation of formaldehyde in the presence of (*Z*)-2-butene (**1**) and examined the ratio of *cis*- to *trans*-1,2-dimethylcyclopropane (CDC/TDC). Table I gives CDC/TDC for a number of experimental conditions along with comparisons of the CDC/TDC obtained by Bader and Generosa[12] in the photolysis of diazomethane and **1** at various pressures.

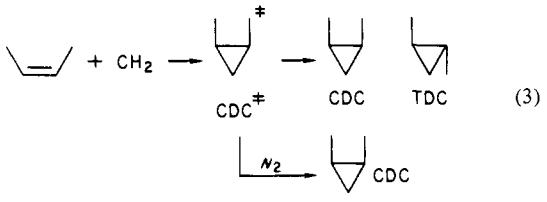
The addition of $O_2$, an efficient scavenger of $C(^3P)$,[13] allows an evaluation of the spin state of the deoxygenating carbon atom. A comparison of entries 1 and 2 in Table I demonstrates that the addition of 10% $O_2$ does not change either the yields of the dimethylcyclopropanes or CDC/TDC within experimental error. This result strongly indicates that the deoxygenating carbon is not $C(^3P)$ and that $CH_2(^3B_1)$ is not generated.

Entry 3 in the table shows that the stereospecificity of the $CH_2$ addition increases when 200 torr of $N_2$ is added. This is the usual pressure effect observed in singlet $CH_2$ additions and is generally ascribed to collisional deactivation of vibrationally excited *cis*-1,2-dimethylcyclopropane (CDC$^*$) as shown in eq 3.[14] In fact,

Table II. Product Ratios of the Reaction of $CH_2$ with Cyclohexene

| reactants | product ratios | | |
|---|---|---|---|
| 1. C + $CH_2O$ + c-$C_6H_{10}$[b] | 1 | 0.75 | 1.63 |
| 2. C + $CH_2O$ + c-$C_6H_{10}$ + $O_2$ (1.9 torr) | 1 | 0.71 | 1.70 |
| 3. C + $CH_2O$ + c $C_6H_{10}$ + $N_2$ 200 torr) | 1 | 0.29 | 1.6 |
| 4. $CH_2N_2$ + c-$C_6H_{10}$[d] | 1 | 0.32 | 1.71 |

[a] All C atom reactions were run using 4.1 mmol of 5-diazotetrazole and 7 torr each of $CH_2O$ and cyclohexene. [b] Cyclohexene. [c] 3- and 4-methylcyclohexene were incompletely separated under the conditions of the gas chromatography. [d] Reference 18, total pressure = 12 torr.



(3)

the increase in stereospecificity exactly parallels that observed by Bader and Generosa[12] upon addition of 200 torr of $N_2$ to the diazomethane–(*Z*)-2-butene system (entries 6 and 7, Table I).

However, in the present case there is sufficient energy for the production of $CH_2(^1B_1)$, and the $N_2$ could serve the dual function of deactivating CDC$^*$ *and* degrading $CH_2(^1B_1)$ to $CH_2(^1A_1)$. In order to test this possibility, we have increased the pressure of the (*Z*)-2-butene anticipating efficient deactivation of CDC$^*$ but reaction of any $CH_2(^1B_1)$ present. The results of this experiment, using 200 torr of **1**, (entry 4, Table 3) are dramatically different from those of Bader and Generosa[12] at the same pressure of **1** (entry 8). In the diazomethane photolysis which generates $CH_2(^1A_1)$, the increased pressure of **1** acts to efficiently deactivate CDC$^*$ and increases the stereospecificity markedly. In the present study, however, increasing the pressure of **1** has no effect on the CDC/TDC, which remains identical with that observed at low pressures of **1**. A further increase in the (*Z*)-2-butene pressure to 620 torr again leaves CDC/TDC unaffected (entry 5).

The large exothermicity of eq 1 raises the possibility that the reactive $CH_2$ is simply the $^1A_1$ state with a great deal of excess energy. If this is the case, the nonstereospecificity at the high (*Z*)-2-butene pressures can be explained by assuming that CDC$^*$ rearranges to TDC at a rate considerably faster than the collisional deactivation rate. Simmons and Taylor[15] have evaluated the rate

(7) For recent reviews of the chemistry of atomic carbon, see: (a) Skell, P. S.; Havel, J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97–105. (b) Mackay, C. In "Carbenes"; Moss, R. A., Jones, M., Jr.; Eds.; Wiley-Interscience: New York, 1975; Vol. II pp 1–42. (c) Shevlin, P. B. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, **1980**, Vol I, pp 1–36.

(8) The $\Delta H_f$ of $CH_2(^3B_1)$ is taken as 93.6 kcal/mol.[9] The uncertainties in the exothermicities of $CH_2(^1A_1)$ and $CH_2(^1B_1)$ formation result from the current controversy regarding the $CH_2(^3B_1)$–$CH_2(^1A_1)$ energy gap.[10] The $^1B_1 \leftarrow {}^1A_1$ excitation energy is taken as 21.1 kcal/mol from the work of Herzberg and Johns.[11]

(9) Lengel, R. K.; Zare, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 7495–7499.

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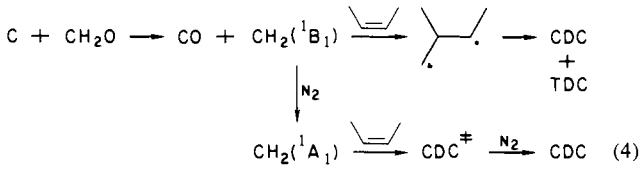
(14) Frey, H. M. *Proc. R. Soc. London, Ser. A*, **1959**, 251, 575–587.

constant for CDC‡ → TDC‡ ($k_g$) as a function of the energy of CDC‡. If one assumes that the $CH_2$ carries away 30% of the exothermicity of eq 1,[16] the data of Simmons and Taylor[15] lead to the conclusion that the energy of CDC‡ is ≃ 129 kcal/mol and that $k_g \simeq 2 \times 10^9$ s$^{-1}$. However, the collisional frequency at 620 torr of (Z)-2-butene is on the order of $1.8 \times 10^{10}$ s$^{-1}$, and a pressure effect on stereochemistry would be expected if highly energetic $CH_2(A_1)$ were the reactive species.

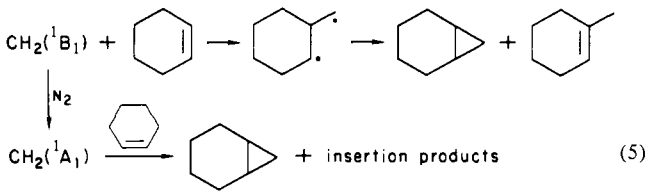
Thus these results are consistent with the formation of $CH_2(^1B_1)$ in the C atom deoxygenation of $CH_2O$. This $CH_2(^1B_1)$ is degraded to $CH_2(^1A_1)$ by $N_2$ but reacts with **1** in a nonstereospecific manner (eq 4) as predicted by Hoffmann.[2] The postulated degradation




(4)

of $CH_2(^1B_1)$ to $CH_2(^1A_1)$ by $N_2$ is consistent with earlier observations by Herzberg[17] who reports that $CH_2(^1A_1)$ is only detectable in the flash photolysis of diazomethane when 200 torr of $N_2$ is added to degrade an initial excited species.

The reaction of deoxygenatively produced $CH_2$ with cyclohexene (eq 2) also indicates a $CH_2$ of different reactivity than that which has been previously observed. Table II compares the present results with those obtained by Rose, Haas, Powers, and Whitney[18] in the gas-phase photolysis of diazomethane with cyclohexene. It is particularly interesting that the product ratios, which have previously been demonstrated to be independent of pressure,[18] differ in the two reactions. In particular, there is far more 1-methylcyclohexene generated in the reactions of deoxygenatively produced $CH_2$ with cyclohexene than in the reactions of $CH_2$ formed from diazomethane. This fact is consistent with the production of $CH_2(^1B_1)$, which undergoes addition via a biradical (eq 5). Addition of $N_2$ serves to degrade the $CH_2(^1B_1)$ to




(5)

$CH_2(^1A_1)$, which adds to cyclohexene to generate products in a ratio strikingly similar to that observed by Rose et al.[18]

Although these results do not require the intermediacy of $CH_2(^1B_1)$, they strongly indicate the presence of a nontriplet $CH_2$ or methylene transfer agent that is degraded to $CH_2(^1A_1)$ by $N_2$ and reacts with alkenes to generate cyclopropanes by a biradical mechanism. Although we cannot absolutely rule out the possibility that this high-energy species is some sort of a complex between C and $CH_2$=O, it seems unlikely that such a complex would live long enough to undergo second-order reaction with an alkene. Skell and Plonka[6a] find no evidence that a complex between C and carbonyl compounds is stable at 77 K. We are continuing to investigate the possiblity that deoxygenation of carbonyl compounds can provide a nonphotochemical route to excited singlet carbenes.

**Acknowledgment.** Support of this research by the National Science Foundation under Grant CHE-8103034 is gratefully acknowledged.

**Registry No. 1**, 590-18-1; $CH_2$, 2465-56-7; C, 7440-44-0; $CH_2O$, 50-00-0; 5-diazotetrazole, 86457-85-4; cyclohexene, 110-83-8.

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(16) It has been estimated that $CH_2$ carries away 30% of the excess energy in diazomethane photolysis.[15]
(17) Herzberg, G. *Proc. R. Soc. London, Ser. A* **1961**, *262*, 291-317.
(18) Rose, T. L.; Haas, A. E.; Powers, T. R.; Whitney, J. M. *J. Phys. Chem.* **1976**, *80*, 1653-1657.

## Cesium 18-Crown-6 Compounds. A Crystalline Ceside and a Crystalline Electride

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We recently[1] reported the isolation of crystals of stoichiometry Cs(18C6) from solutions of cesium and 18-crown-6 (18C6) in a 2-aminopropane–diethyl ether mixture in the presence of dissolved lithium. Although the "sandwich" ceside, $Cs^+(18C6)_2{\cdot}Cs^-$, could not be ruled out, the properties suggested that this crystalline compound was an electride, $Cs^+(18C6){\cdot}e^-$. The strongest argument for the latter assignment was the optical transmission spectrum of a thin solvent-free film. As shown in Figure 1, this film initially had absorptions from both $Cs^-$ and trapped electrons ($e_t^-$) but with time the absorption due to $Cs^-$ decreased and that due to $e_t^-$ increased. This suggested that the *electride* is the thermodynamically stable form. In addition, the compound $Cs^+(18C6){\cdot}Na^-$ had been isolated[2] so we reasoned that a ceside would have the stoichiometry $Cs_2(18C6)$, ($Cs^+(18C6){\cdot}Cs^-$), rather than Cs(18C6). The susceptibility, EPR spectra and electrical conductivity were compatible with either an electron-doped ceside or a largely spin-paired electride. Spin pairing in electrides had been observed previously[3,4] so the nearly diamagnetic susceptibility was not surprising. While the band gap of 0.8 ± 0.1 eV obtained from powder conductivities was too small for a pure ceside, it could result from electrons trapped at $Cs^-$ vacancies. In fact, extrapolation of the conductivity to infinite temperatures gives a limiting specific conductance of only about 1 $\Omega^{-1}$ cm$^{-1}$, which suggests extrinsic semiconductivity.

In spite of the evidence in favor of the simple electride $Cs^+(18C6){\cdot}e^-$, the ceside $Cs^+(18C6)_2{\cdot}Cs^-$ could not be ruled out since "sandwich" complexes of $Cs^+$ with crown ethers exist in solution[5] and in solid salts.[6] We reasoned that if Cs(18C6) is the ceside $Cs^+(18C6)_2{\cdot}Cs^-$ then it might be possible to synthesize the corresponding electride $Cs^+(18C6)_2{\cdot}e^-$ by appropriate choices of solvents and solution composition. Black, shiny crystals were prepared by the same method used for Cs(18C6) but with a 1:2 mol ratio of cesium to 18C6. Both types of crystals were also precipitated from mixtures of dimethyl ether and trimethylamine in the absence of lithium.

Analysis of the new crystals by the methods described previously[1,2] showed that they have the stoichiometry $Cs(18C6)_2$, immediately suggesting that this compound is the electride $Cs^+(18C6)_2{\cdot}e^-$. The optical spectrum of a thin film obtained by dissolving the crystals in methylamine and evaporating the solvent from a liquid film as with other alkalides and electrides[7-9] is shown in Figure 1. Only a single narrow peak at 6700 cm$^{-1}$, independent of time, was observed, as expected for an electride.

Magnetic susceptibility measurements[10] on a sample of this compound showed that it is strongly paramagnetic with a Cu-

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(9) Dye, J. L.; DaGue, M. G.; Yemen, M. R.; Landers, J. S.; Lewis, H. L. *J. Phys. Chem.* **1980**, *84*, 1096.
(10) Issa, D.; Ellaboudy, A.; Janakiraman, R.; Dye, J. L. unpublished results.

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