°C giving distinct EPR spectra that were attributed to water structure changes upon freezing. The presence of two differently oriented oxygen ligands in crystals of this molecule at 77 K and their equilibration to one species at 125 K has already been cited.[4] Therefore, a more general statement is that there exist conformational substates of the protein and that freezing traps the molecule in two minima of nearly equal energy. In our CoCPA data, the appearance of the second feature would require some rearrangement of ligands. For the second site, the g value in the direction corresponding to $g = 2.0$ for the first complex is about 4.4. We note that CuCPA is devoid of esterase and peptidase activity whereas CoCPA is active. The absence of extra sites in the single crystals of CuCPA may be related to an inability of the metal complex to rearrange to accommodate substrates in a way that can be done by CoCPA. The inactivity of CuCPA may of course be related to a number of other "inappropriate" ligation properties of Cu. Our results suggest that a temperature-dependent study of the X-ray crystallography of CoCPA and ZnCPA would show a dynamism of the metal coordination sphere and related protein structural changes.

Acknowledgment. We are grateful to Professor J. S. Wood for discussions and for obtaining the precession photographs.

Registry No. Carboxypeptidase A, 11075-17-5.

Communications to the Editor

Reaction of Carbethoxycarbene with *o*-Carborane[1]

Guo-xiu Zheng[2] and Maitland Jones, Jr.*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received March 23, 1983

Nearly a century ago, Buchner and Curtius examined the thermal decomposition of ethyl diazoacetate in benzene.[3] It took much of the next hundred years to unravel the structures of the "Buchner esters".[4] It is now known that reaction of carbenes with benzene and other aromatic compounds proceeds by initial formation of the bicyclo[4.1.0] system (norcaradiene) which usually,[5] but not always,[6] opens to the related cycloheptatriene. The addition products are accompanied by smaller amounts of the products of carbon-hydrogen insertion. Methylene gives 9% toluene and 32% cycloheptatriene in its reaction with benzene.[7] Other carbenes give insertion products, but some of these compounds may be formed by rearrangements of norcaradienes.[8]

Benzene has a set of three-dimensional aromatic cousins in the icosahedral carboranes of which **1**, *o*-carborane, is the most accessible. Molecular orbital treatments yield a set of 13 bonding MO's, which are nicely filled by the available 26 electrons. Alternatively, **1** may be viewed as a combination of two caps and two five-membered rings.[9,10] A total of six electrons is contributed to "interstitial" bonding in the three-dimensionally aromatic system, Aromaticity is reflected in substantial thermal stability as well as traditionally "aromatic" chemical properties such as the ability to do aromatic substitution reactions.[11] Having already begun a study of the properties of divalent carbon attached to a carborane,[12] we wondered if carbenes would react with carboranes as they do with the "two-dimensionally" aromatic benzene. We chose to examine the generation of the well-studied carbethoxycarbene[5,13] with **1**.

Table I. Insertion of Carbethoxycarbene into the B-H Bonds of 1 vs. Calculated Framework Charges

	6	2	3	4	5
	C-H (1,2)	B-H (3,6)	B-H (4,5,7,11)	B-H (8,10)	B-H (9,12)
$h\nu$	0	4	19	29	47
Δ	0	3	19	27	52
Δ/CuCl	0	5	29	20	46
group charges[17]	+0.07	+0.03	0.00	-0.05	-0.05

Irradiation of ethyl diazoacetate in a hexafluorobenzene solution of **1** led to four products (**2**-**5**) (Scheme I), along with small amounts of ethyl fumarate, ethyl maleate, and, in the thermal reaction, hexafluorobenzene/carbene adducts. Separation of the four isomers was satisfactorily accomplished on a 6.5 ft × $^{1}/_{4}$ in. 15% QF-1 on 60/80 Chromosorb W column operated at 195 °C. Thermal decomposition of a hexafluorobenzene solution of **1** and ethyl diazoacetate in the presence or absence of CuCl led to the same four adducts. Table I gives the ratios as determined by gas chromatography, after reaction for 1 h.[14]

GC/MS showed that **2**-**5** incorporated the elements of the carbene and **1**. Precise mass spectrometry established the formulae as $C_6B_{10}H_{18}O_2$. ^{1}H NMR and infrared spectroscopy revealed that the ester function was retained, and ^{11}B NMR at 115.5 and 80.25 MHz permitted a detailed structural analysis.[15] The compounds

---

(1) Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant CHE-81-01212) is gratefully acknowledged. Zheng, G.-x.; Sung, D. D.; Gallucci, R. R.; Chari, S. L.; Chiang, S.-H.; Jones, M., Jr. "Abstracts of Papers", 186th meeting of the American Chemical Society, Washington, D. C., Aug-Sept 1983, American Chemical Society: Washington, D.C., 1983; ORGN 0117.

(2) On leave from the Institute of Chemistry, Academia Sinica, Beijing, People's Republic of China.

(3) Buchner, E.; Curtius, T. *Ber. Dsch. Chem. Ges.* **1885**, *18*, 2377.

(4) Doering, W. von E.; Laber, G.; Vonderwahl, R.; Chaimberlain, N. F.; Williams, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 5448.

(5) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971; Vol. 2.

(6) Ciganek, E. *J. Am. Chem. Soc.* **1967**, *89*, 1454.

(7) Doering, W. von E.; Knox, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 297.

(8) Reference 5, p 227 ff.

(9) Jemmis, E. D. *J. Am. Chem. Soc.* **1982**, *104*, 7017.

(10) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781.

(11) (a) Grimes, R. N. "Carboranes"; Academic Press: New York, 1970. (b) Onak, T. "Organoborane Chemistry"; Academic Press: New York, 1975. (c) Beall, H. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975; Chapter 9. For examples, see: Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1966**, *5*, 1471, 1478, 1483 (*o*-carborane). Stanko, V. I.; Klimova, A. I.; Titova, N. S. *Zh. Obshch. Khim.* **1968**, *38*, 2817 (*m*-carborane).

(12) Chari, S. L.; Chiang, S.-H.; Jones, M., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3138.

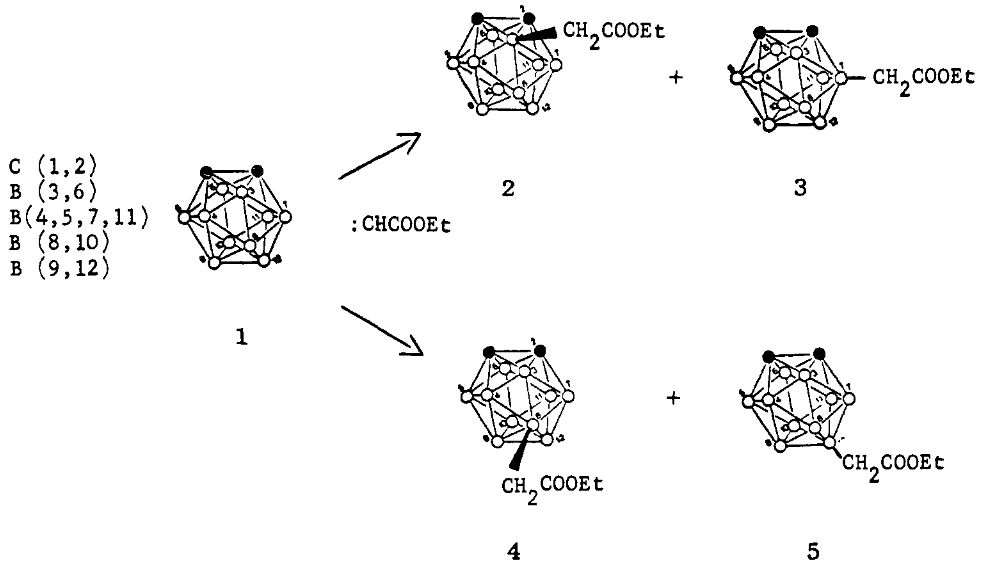
(13) Jones, M., Jr., Moss, R. A., Eds. "Carbenes"; Wiley: New York, 1973; Vol. 1. Moss, R. A., Jones, M., Jr., Eds., "Carbenes"; Wiley: New York, 1975; Vol. 2.

(14) With time the insertion reaction apparently becomes more statistical. We are investigating the causes of this phenomenon and quote the t = 1 h data as our best approximation of the t = 0 h value. The yield of **2**-**5** is about 10% after 1 h and 20% after 40 h. Despite these modest yields the reaction is a useful one as the starting materials are simple and the products rather easy to isolate. At long reaction times GC/MS analysis shows small amounts of compounds formed from one carborane and two or even three carbenes.

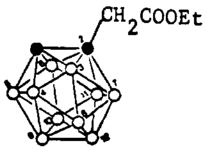
(15) We are most grateful to Professor L. G. Sneddon of The University of Pennsylvania for help in obtaining the high-field ^{11}B spectra and for enlightening conversations about boron. Details of the analysis of spectra are available on request.

0002-7863/83/1505-6487$01.50/0

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.

---

[16] Zakharkin, L. I.; Chapovskii, Yu. A.; Brattsev, V. A.; Stanko, V. I. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1966**, *36*, 892.

[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.

[19] Hawthorne, M. F.; Berry, T. E.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 4746.

[20] Sung, D. D.; Gallucci, R. R., unpublished work.

Possible Involvement of Excited Singlet Methylene in the Deoxygenation of Formaldehyde by Atomic Carbon

Sheikh N. Ahmed and Philip B. Shevlin*

Department of Chemistry, Auburn University
Auburn, Alabama 36849

Received April 29, 1983

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.

[2] Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485.

[3] Zabransky, V. P.; Carr, R. W., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 1130–1135.

[4] Pilling, M. J.; Robertson, J. A. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 968–984.

[5] Dyer, S. F., Shevlin, P. B. *J. Am. Chem. Soc.* **1979**, *101*, 1303–1304.

[6] (a) Skell, P. S.; Plonka, J. H. *J. Am. Chem. Soc.* **1970**, 92, 836–839. (b) Dewar, M. J. S.; Nelson, D. J.; Shevlin, P. B.; Biesiada, K. A. *Ibid.* **1981**, *103*, 2802–2807.

0002-7863/83/1505-6488$01.50/0