Tetrahedron Letters Vol. 21, pp 2851 - 2854
0040-4039/80/0722-2851$02.00/0

A MOLECULAR ORBITAL STUDY OF CARBOMETHOXYCARBENE AND DICARBOXYCARBENE

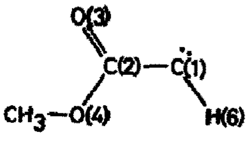
R. Noyori* and M. Yamakawa
Depertment of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan

Summary: The MINDO/3 calculations on the title carbenes suggest that the nonclassical, closed structures are favored in gas phase or under externally unperturbed conditions.

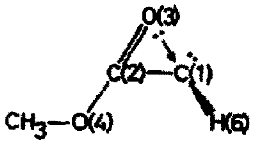
Most carbenes possessing an electron-withdrawing or conjugative substituent(s) have triplet ground state and display radical-type reactivities.[1] However, chemistry of carbalkoxycarbenes,[2] formed by photolytic or thermal decomposition of diazoacetates has not yet

$$ROCOCHN_2 \xrightarrow{h\nu \text{ or } \Delta} ROCOCH: \quad + \quad N_2$$

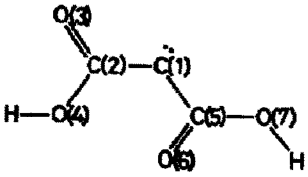
been fully clarified. Recent EPR study on these carbenes in frozen solutions or in vacuum-deposited, rigid matrices indicated triplet ground states.[3] But the chemical behavior is interpreted by assuming that the reacting carbenes are in a singlet manifold. (1) Carbenes of this type cycloadd across olefinic double bonds, producing cyclopropane adducts, in a stereospecific cis manner (Skell's criterion[4]).[5] (2) Aliphatic C—H bonds are susceptible to the carbene insertion reaction; the stereochemical outcome (retention of configuration)[6] and relative reactivities (tert:sec:pri = 3.1—2.9:2.3:1.0)[7] are compatible with the singlet reaction. (3) Carbalkoxycarbenes react with dialkyl sulfides[8] or ethers[9] in an electrophilic manner to give stable S-ylides and unstable O-ylides, respectively. (4) Even in inert solvents these carbenes do not suffer decay to the triplet.[10] (5) In fluid solution, only sensitized photolysis of the diazo precursors allows efficient generation of triplet carbalkoxycarbenes which exhibit radical reactivities.[11, 12] Such intriguing features have prompted us to examine the electronic structures of carbomethoxycarbene (I) and dicarboxycarbene (II) by molecular orbital (MO) calculations with full geometrical optimization.[13]



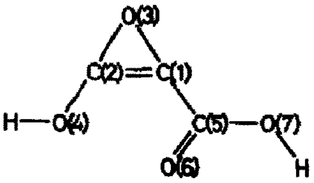
Ia



Ib



IIa



IIb

Molecular geometry of singlet carbomethoxycarbene was determined by the MINDO/3 method.[14] This calculation suggests the classical open form Ia is not species of a local ener minimun, but the geometry optimization led, without activation energy, to the closed structu Ib. The detailed structure is given in Figure 1. The computed ground-state structure Ib is be distinguished from the regular oxirene structure.[15] The C(1) atom (carbenic center) has pyramidal configuration with a nonbonding electron pair; the C(1)—H(6) bond is bent up by the angle of 64° from the C(1)—C(2)—O(3) plane. The C(2) atom has a trigonal, nearly planar structure. The C(1)—C(2) bond distance of 1.391 A is intermediate between an oxirane C—C bond (1.470 A)[16] and an oxirene C=C bond (1.245 A).[17] The C(1)—O(3) bond of 1.507 A is longer than an oxirane C—O bond (1.435 A) and shorter than an oxirene C—O bond (1.550 A).[16,17] The distance of the C(2)—O(3) bond possessing substantial double bond character, 1.306 A, is shorter than associated with oxirane C—O single bonds. The C(2)—O(4) bond (1.281 A) has even higher bond order (cf. standard ester C=O, 1.245 A; C—O, 1.312 A).

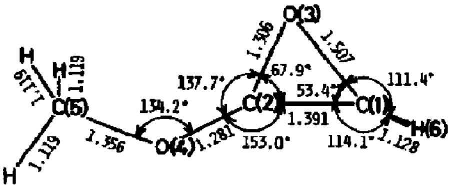
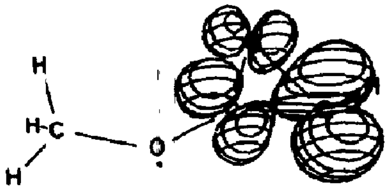
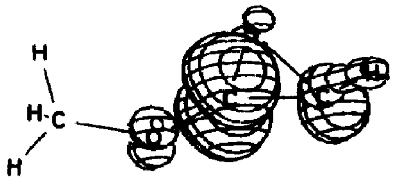


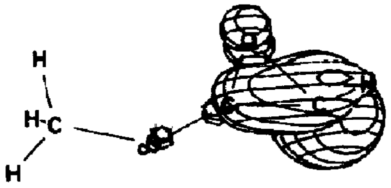
Figure 1. Bond lengths and bond angles of singlet Ib (ΔH_f = -24.5 kcal/mol).



NLUMO (1.38 eV)



LUMO (0.34 eV)



HOMO (-8.45 eV)

Figure 2. Selected MOs of Ib.

The singlet state Ib is calculated to lie 8.9 kcal/mol below the triplet having an equilibrated open geometry.[14] Thus the stabilization of singlet I is not due to conjugation between the nonbonding electron pair of the p^2 carbene and the electron-withdrawing ester substituent as has been postulated earlier.[2b] Rather this is mainly a result of supply of a nonbonding electron pair from the carbonyl oxygen into the vacant p_π orbital of the σ^2 carbene. Synergistic electron back-donation from C(1) to C(2) also contribute to the stabilization to some extent. The C(1) atom in Ib has charge density of -0.085, whereas C(2) is positively charged.

In principle carbenes are ambiphilic. Figure 2 shows the shapes of some selected MOs of Ib which control the reactivity. In going from the hypothetical open form Ia to the closed structure Ib, electrophilicity of the carbenic carbon is decreased because of the electron release from the carbonyl oxygen. The shape of the HOMO predicts the possible nucleophilic reaction at C(1), although such behavior has not yet been recognized by experiments. The electrophilic reaction of Ib takes place by use of the next LUMO in which C(1)—O(3) is antibonding in nature. Nucleophiles such as silfides, ethers, alkenes, would attack the C(1) atom from the side opposite the leaving O(3) atom to give the addition products. This mechanism is reminiscent of the hydrolytic behavior of chiral α-bromopropionate which gives lactate with stereochemical retention; the α-lactone intermediate is structurally closely related to Ib.

Thus the semi-empirical MO calculations favor the nonclassical, closed structure for the carbene I in gas phase or under externally unperturbed conditions, accounting for the great

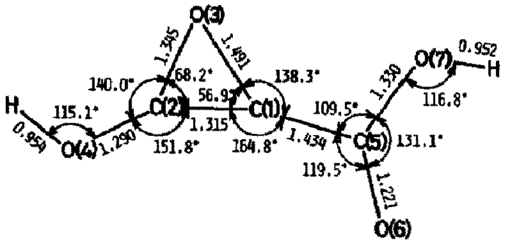


Figure 3. Bond lengths and angles of IIb (ΔH_f = -147.2 kcal/mol).

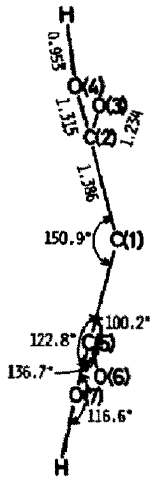


Figure 4. Bond lengths and angles of IIa (ΔH_f = -132.7 kcal/mol).

stability of the singlet manifold. In solution, however, the classical open forms may also exist as a result of stabilization by solvation with surrounding molecules.[18,19]

The MINDO/3 calculation of dicarboxycarbene led to the cyclic form IIb as the optimized ground-state structure. The structural parameters are given in Figure 3. This singlet molecule, unlike Ib, has nearly planar oxirene-type structure. Here the C(1) atom does no longer have a nonbonding electron pair. The singlet-triplet energy separation was calculated to be 7.6 kcal/mol. In addition, we found several open structures with different carboxyl conformation as local energy minima. A typical example is the σ^2 singlet carbene IIa bearin two equivalent carboxyl groups (Figure 4), which lies 14.5 kcal/mol above IIb.

REFERENCES AND NOTES

1. W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, 1971; M. Jones Jr., and R. A. Moss, "Carbenes", Vol. 1 and 2, John Wiley, New York, 1973 and 1975.
2. Reviews: (a) V. Dave and E. W. Warnhoff, Org. Reac., 18, 217 (1970); (b) A. P. Marchand and N. MacBrockway, Chem. Rev., 74, 431 (1974).
3. R. S. Hutton and H. D. Roth, J. Am. Chem. Soc., 100, 4324 (1978).
4. P. S. Skell and R. C. Woodworth, J. Am. Chem. Soc., 78, 4496 (1956).
5. W. von E. Doering and T. Mole, Tetrahedron, 10, 65 (1960). See also footnote 3 in T. DoMinh and O. P. Strausz, J. Am. Chem. Soc., 92, 1766 (1970).
6. Footnotes 65 and 174 in ref 2b.
7. W. von E. Doering and L. H. Knox, J. Am. Chem. Soc., 78, 4947 (1956); ibid., 83, 1989 (1961).
8. W. Ando, Acc. Chem. Res., 10, 179 (1977).
9. H. Nozaki, H. Takaya, and R. Noyori, Tetrahedron Lett., 2563 (1965); Tetrahedron, 22 3393 (1966); H. Iwamura, Y. Imahashi, K. Kushida, K. Aoki, and S. Satoh, Bull. Chem. Soc. Jpn., 49, 1690 (1976).
10. Footnote 65 in ref 2b.
11. H. D. Roth, Acc. Chem. Res., 10, 85 (1977).
12. Sensitized photolysis of methyl diazomalonate generates triplet dicarbomethoxycarbene; M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, Jr., P. M. Lowley, K. F. Hummel, and D. S. Malament, J. Am. Chem. Soc., 94, 7469 (1972).
13. Previous MO calculations on carbalkoxycarbenes (a) (Extended Hückel method) D. E. Thornton, R. K. Gosavi, and O. P. Strausz, J. Am. Chem. Soc., 92, 1768 (1970); I. G. Csizmadia, H. E. Gunning, R. K. Gosavi, and O. P. Strausz, ibid., 95, 133 (1973); (b) (MINDO/3) R. Noyori, M. Yamakawa, and W. Ando, Bull. Chem. Soc. Jpn., 51, 811 (1978).
14. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Am. Chem. Soc., 97, 1285 (1975); QCPE (Quantum Chemistry Program Exchange) No. 309.
15. The oxirene participation has been suggested in the gas-phase photolysis of methyl diazo acetate.[13a]
16. T. E. Turner and J. A. Howe, J. Chem. Phys., 24, 924 (1956).
17. O. P. Strausz, R. K. Gosavi, A. S. Denes, and I. G. Csizmadia, J. Am. Chem. Soc., 98, 4784 (1976).
18. The triplet carbenes possessing an open structure has been calculated to be the more stable than the singlet entities.[13b]
19. The closed form Ib would be an intermediate in the carbene rearrangements in vapor phase.[13a]

(Received in Japan 14 April 1980)