STERIC COURSE OF THE ADDITION OF MONOCHLORO-
CARBENOID[1] TO SOME BRIDGED BICYCLIC OLEFINS[2]

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The pattern of product composition obtained by the addition of monosub-
stituted carbenes (CHX) to "unsymmetric" acyclic and monocyclic olefins is
well established.[3]   Anti stereoselectivity is generally displayed by car-
balkoxy, aryloxy and alkoxycarbenes, whereas phenyl, phenylthio, phenylseleno
and chlorocarbenes exhibit preferential syn addition.[4]

We now report, in striking contrast, that the addition of chlorocarben-
oid to bridged bicyclic olefins proceeds exo with dominant anti orientation.
Chlorocarbene was allowed to react with bicyclo[2.2.2]octene-2 (I), norbor-
nene (II), its 1-methyl (III) and 2-methyl (IV) derivatives and finally cy-
cloheptene (V) by way of comparison.[1,5]

For the three norbornenes (II - IV), only exo-anti and rearranged exo-
syn adducts were detected.   Rearrangement had occurred stereospecifically
to produce their exo-4-chlorobicyclo[3.2.1]octene-2 derivatives.[6,7]
Bicyclo[2.2.2]octene-2 gave syn and anti adducts, of which the former had
undergone rearrangement[6] to 2-chlorobicyclo[3.2.2]nonene-3.   However,
rearrangement where and when it occurred arose solely from the syn adduct[7,8]
and accordingly syn-anti ratios (see Table) were estimated without diffi-

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culty by integration of the appropriate n.m.r. signals of the reaction mix-
tures.[9]   As the results in the table show, the syn-anti ratios are the
reverse of those usually encountered for a monocyclic olefin (cf. I and V).

   Although electronic or hyperconjugative effects should not be discounted,
especially where acyclic or monocyclic olefins are concerned, the more impor-
tant factor in determining syn-anti adduct ratios is probably the delicate
balance between steric repulsion and attraction in the transition state for
addition.[10]   For example, the transition states for the interaction of
monochlorocarbene and cis-butene leading to syn and anti products may be com-
pared to the gauche and trans conformations of n-propyl chloride.   The for-
mer conformation is favored because of van der Waal's attractive forces bet-
ween the chlorine atom and the methyl group.[11]   Typically, the 3:1 syn-
anti ratio observed in the addition to cycloheptene (V) reflects the domin-
ance of such attractive effects.

   In bicyclo[2.2.2]octene-2 and the norbornenes, hyperconjugative effects
should be negligible due to the restrictions dictated by the geometry of
these bridged molecules.   Therefore, dispersion forces should be left to
decide the product ratio.   It is remarkable that chlorocarbene adds to
bicyclo[2.2.2]octene-2 (I) in a 1:5 syn-anti ratio.   Evidently bicyclo-
[2.2.2]octene-2, unlike cycloheptene, possesses a steric feature, undoubtedly
the ethane bridge, which tips the balance between attractive and repulsive
forces.[14]

   Norbornene (II) presents a more complex stereochemical situation.   In
addition to steric factors which alone decide syn-anti ratios, there could be
stereoelectronic[12] and torsional factors[13] which influence the exo to
endo addition ratio.   The result is that addition occurs exclusively exo.
Little exo-syn product is formed, somewhat less than for bicyclo[2.2.2]oct-
ene-2, undoubtedly owing to the attendant severe flagpole-type repulsions
which divert the incoming chlorocarbene to the sterically more congenial exo-
anti addition mode.[14]

   A similar stereochemical outcome was observed with 1-methyl (III) and 2-

TABLE

Stereoselectivity of the Addition of Monochlorocarbene
### to Various Olefins (I - IV)

Olefin	Syn/Anti Ratio
I	1:5
II	1:6
III	1:1.5
IV	1:9.8
V	3:1

methylnorbornenes (IV).   However, substitution by methyl has a marked influ-
ence on the syn-anti ratios.   Placing methyl at C_1 on norbornene has caused
a sizeable swing to syn addition which is presumably induced by the van der
Waal's attraction between the methyl group and chlorine atom of the incoming
chlorocarbene species.   On the other hand, when methyl is switched to C_2,
dispersion forces strongly favor the anti addition.

The absence of endo addition to norbornene is doubly surprising; firstly,
in view of the ready addition of chlorocarbene to bicyclo[2.2.2]octene-2 which
appears to be a reasonable model for the endo side of norbornene; and se-
condly, because both the endo-anti and endo-syn addition modes appear to be
free of the steric disability suffered on exo-syn addition.

Recently, it was broadly suggested that the dominant exo cyclopropana-
tion of norbornene can be explained in terms of torsional interactions.[13]
It appears from models that oppositions between the C_1-H and C_2-H bonds (and
C_3-H and C_4-H bonds) will be decreased on exo addition (VI) and increased on
endo addition (VII).   However, exo addition also involves severe Pitzer
strain between the syn disposed C_7 and carbene bonds, which will militate
against exo addition.[15]   Accordingly, it is difficult to see how exclusive
exo addition can be rationalized by torsional interactions especially if

steric factors (cf. those operating in exo-syn addition) are counted as well. Therefore the reason for the exclusive exo course of addition is probably due to a stereoelectronic factor.
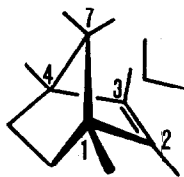
VI   VII
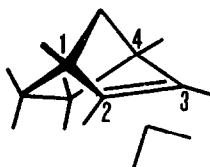
Acknowledgement

References

1. For convenience, we employ the terms carbene and carbenoid indifferently. However, the interaction of methylene chloride and methyllithium leads, most probably, to dichloromethyllithium which subsequently undergoes addition to the double bond rather than free chlorocarbene. (cf.G.L.Closs and J.J. Coyle, J. Am. Chem. Soc., 87, 4270 (1965).

2. Part XIII of a series entitled "The Stereochemistry of Bicyclo[3.2.1]-octane"; for preceding paper see C.W. Jefford and E. Huang Yen, Tetrahedron, (1967) in the press.

3. By "unsymmetric" is meant an olefin which has neither a center of symmetry nor a plane of symmetry coincident with the π orbital plane.

4. W. Kirmse, Carbene Chemistry, Academic Press, New York, 1964, Chap. 12.

5. Methyllithium was prepared from methyl chloride and used in ethereal solution (1.6 - 1.7 M). In all cases, methyllithium (0.80 M) was added to a mixture of methylene chloride (0.75 M) and olefin (1.00 M).

(cf. G.L. Closs and L.E. Closs, J. Am. Chem. Soc., 82, 5723 (1963)).

6.   C.W. Jefford, S. Mahajan, J. Waslyn and B. Waegell, J. Am. Chem. Soc.,
     87, 2183 (1965).

7.   C.W. Jefford, E. Huang Yen and R.T. Medary, Tetrahedron Letters, No.51,
     6187 (1966); C.W.Jefford & R.T. Medary, Tetrahedron, 23, 4123 (1967).

8.   L. Ghosez, P. Laroche and G. Slinckx, Tetrahedron Letters, No. 29, 2767
     (1967); L. Ghosez, G. Slinckx, M. Glineur, P. Hoet and P. Laroche,
     ibid., No. 29, 2773 (1967).

9.   Details of the rearrangement will be found in the accompanying communi-
     cation.

10. a) G.L. Closs, R.A. Moss and J.J. Coyle, J. Am. Chem. Soc., 84, 4985
        (1962); G.L. Closs and R.A. Moss, ibid., 86, 4042 (1964);
        U. Schöllkopf and J. Paust, Chem. Ber., 98, 2227 (1965);
     b) R.A. Moss, J. Org. Chem., 30, 3261 (1965).

11. Y. Morino and K. Kutchitsu, J. Chem. Phys., 28, 175 (1958);
     N. Sheppard, Adv. Spectr., 1, 295 (1959);
     T.N. Sarachman, J. Chem. Phys., 39, 469 (1963).

12. Preferential bond formation on the exo side of norbornene could be due
     to better overlap with the exo than the endo lobes of p-orbitals on C_2
     and C_3.

13. a) P. v R. Schleyer, J. Am. Chem. Soc., 89, 699 (1967);
     b) P. v R. Schleyer, ibid., 89, 701 (1967).

14. Another striking example of steric interactions reversing the usual
     stereoselectivity order is provided by p-tolylcarbenoid and t-butyl-
     ethylene which give mainly trans adduct (ref. 10b).

15. Generally aryl and aroyl azides add to norbornenes to form the exo tri-
     azoles ("Azide Formation" sic ref. 13b) which subsequently lose nitrogen
     to form exo aziridines.   However, cases of predominant formation of
     endo aziridine have also been reported (L.H. Zalkow and C.D. Kennedy,
     J. Org. Chem., 28, 3309 (1963), and A.C. Oehlschlager and L.H. Zalkow,
     Chem. Comm., 5, (1966)).