

## The Addition of Halocarbenes to Bridged Bicyclic Olefins\*

By C. W. JEFFORD

Institut de Chimie Organique, Ecole de Chimie, Université de Genève, 1211 Genève 4

### Summary

It is well known that halocarbenes add stereospecifically to olefins to yield halocyclopropanes which undergo, in appropriate cases, rearrangement to allylic halides. When a bridged bicyclic olefin, such as norbornene is used, these reactions take on new dimensions from the mechanistic and synthetic point of view. The rigid geometry and symmetry of the olefin enable significant information to be obtained on both the nature of the addition and the subsequent rearrangement processes. The behavior of monohalo- and dihalocarbenes (e.g. CHX and CX<sub>2</sub> where X = Cl, Br and F; and CXY where X = F and Y = Cl, Br) has been investigated with respect to substituted norbornenes, bicyclo [2.2.2]octene-2 and bicyclo [3.2.1]octene-2.

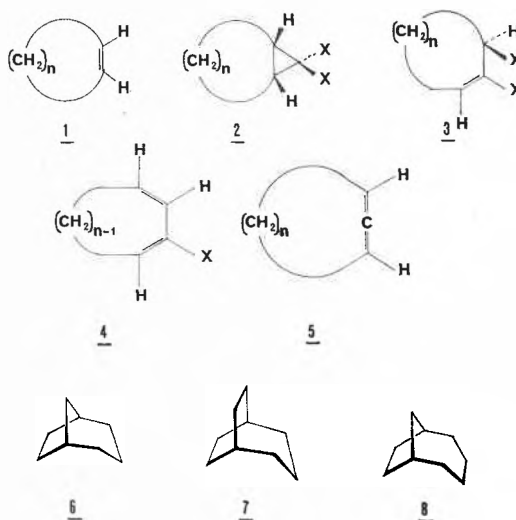
The role of attractive and repulsive forces on the orientation of the carbene addition to the double bond is discussed. The rearrangement process, which is uniquely controlled by the geometric constraint imposed on the cyclopropane adduct and by the configuration of its substituents, is most completely described by the DEWAR-ZIMMERMAN rules.

The addition of halocarbenes to such freely available bridged bicyclic olefins permits convenient synthesis of their less accessible higher homologues.

### Introduction

The addition of dihalocarbenes to olefins is by now a familiar method for the direct incorporation into a molecule of a single carbon atom which can be subsequently modified. The first step is the formation of a dihalocyclopropane adduct, which can react in several ways<sup>1</sup>. Under appropriate circumstances, the adduct from a monocyclic olefin (1) can be induced to rearrange either without (2 → 3) or with elimination of one molecule of hydrogen halide (2 → 4) or by reductive dehalogenation (2 → 5)<sup>2,3</sup>. Thus, allylic derivatives and dienes are, in principle, available for further synthetic exploitation.

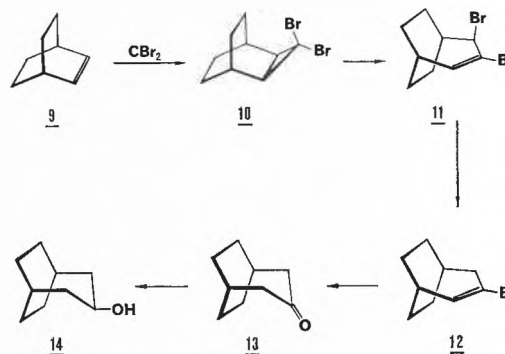
Some time ago we became interested in the chemistry of conformationally constrained common rings, such as bicyclo [3.2.1]octane (6) bicyclo [3.2.2] nonane (7) and bicyclo [4.2.1]nonane (8)<sup>4</sup>. A simple method for their synthesis was needed from easily accessible precursors.



It appeared, at least on paper, that the carbon skeletons of 6, 7 and 8 could be constructed by the addition of dihalocarbene to norbornene, bicyclo [2.2.2]octene-2 and bicyclo [3.2.1]octene-2 respectively, since all three olefins were freely available. Indeed, not only was the immediate objective of synthesis attained but important insights were obtained into the stereochemical requirements of the addition step and the attendant rearrangement and eliminative processes.

### Dihalocarbenes and Bridged Bicyclic Olefins

The addition of dibromocarbene to bicyclo [2.2.2]octene-2 (9) typifies the general synthetic procedure for making constrained common rings. The cyclopropane adduct (10), which is first formed, is unstable under the experimental conditions and rearranges spontaneously to 3,4-dibromobicyclo [3.2.2]nonene-2 (11).



S. MAHAJAN and K. C. RAMEY, *Chem. Comm.* 1966, 616; f) C. W. JEFFORD, S. MAHAJAN, R. T. MEDARY, W. WOJNAROWSKI, B. WAEGELL and K. C. RAMEY, *Chem. Comm.* 1967, 310.

\* Presented at the Halocarbene Symposium, American Chemical Society Meeting, Chicago (Illinois) September 14-18, 1970.

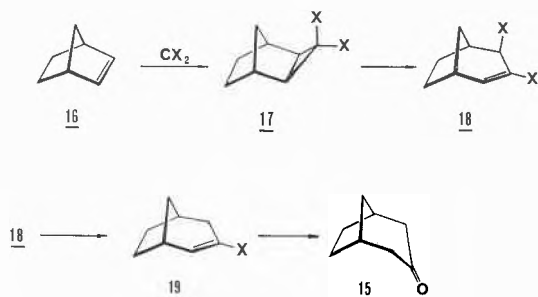
<sup>1</sup> a) W. E. PARHAM and E. E. SCHWEIZER, *Organic Reactions* (A. C. COPE, Editor) Vol. XIII, Chap. 2, J. Wiley and Sons Inc, New York, London 1963; b) W. KIRMSE, *Carbene, Carbenoide und Carbenanalogie*, Verlag Chemie, Weinheim (Bergstraße) 1969; c) R. BARLET and Y. VO-QUANG, *Bull. Soc. Chim. France* 1969, 3729.

<sup>2</sup> a) S. R. SANDLER, *J. Org. Chem.* 32 (1967) 3876; b) R. FIELDS, R. N. HASZELDINE and D. PETER, *J. Chem. Soc. (C)* 1969, 165.

<sup>3</sup> a) M. S. BAIRD, D. G. LINDSAY and C. B. REESE, *J. Chem. Soc. (C)* 1969, 1173; b) T. ANDO, H. HOSAKA, H. YAMANAKA and W. FUNASAKA, *Bull. Chem. Soc. Japan* 42 (1969) 2013.

<sup>4</sup> a) C. W. JEFFORD and B. WAEGELL, *Tetrahedron Letters* No 28 (1963) 1981; b) B. WAEGELL and C. W. JEFFORD, *Bull. Soc. Chim. France* 1964, 844; c) C. W. JEFFORD, J. GUNSHER and B. WAEGELL, *Tetrahedron Letters* No 38 (1965) 3405; d) C. W. JEFFORD, D. T. HILL and J. GUNSHER, *J. Amer. Chem. Soc.* 89 (1967) 6881; e) C. W. JEFFORD,

The allylic halogen is removed smoothly from **11** by means of lithium aluminum hydride and the resulting vinyl bromide (**12**) on hydrolysis yields the ketone (**13**) which may be reduced to the alcohol (**14**). The poor yield (4% when bromoform is used as precursor) for the initial addition step is more than compensated by the fact that a single product is obtained, unadulterated with isomers<sup>5</sup>. This advantage is nicely illustrated in the synthesis of bicyclo [3.2.1]octanone-3 (**15**) by the same route. Other methods are available for preparing **15**, for example, by oxidation of the alcohols obtained by the action of nitrous acid on 2-aminomethylnorbornane or oxidative hydroboration of bicyclo [3.2.1]octene-2, however mixtures of **15** with its isomers are formed<sup>6, 7</sup>. Norbornene (**16**), true to form, undergoes addition of dichloro or dibromocarbene exclusively on the *exo* side. Significantly, the adduct (**17**) rearranges to *exo*-3,4-dihalobicyclo [3.2.1]octene-2 (**18**).



Reduction of **18** to 3-halobicyclo [3.2.1]octene-2 (**19**) followed by hydrolysis affords the ketone **15** in an overall yield of 59% when dichlorocarbene is generated by the interaction of sodium methoxide and ethyl trichloroacetate<sup>8</sup>. The remarkable features of the addition and rearrangement are that they both occur with *exo* stereospecificity<sup>5, 9</sup>. The stereochemistry of the latter step could be accommodated by the formation of the ion pair (**21**) which arises by rupture of the C2-C4 and the C-Z or C-Y bonds of the cyclopropane precursor (**20**). Subsequent annihilation of charge could take place by attack of the anion Z<sup>-</sup> at C2 or C4 to the same extent. In agreement with this idea, the addition of dichloro- and dibromocarbenes to 1-methylnorbornene-2 (**23**) gives both isomers (**25** and **26**) by rearrangement of the symmetrical precursive cyclopropane adduct (**24**) which, however, is not isolated.

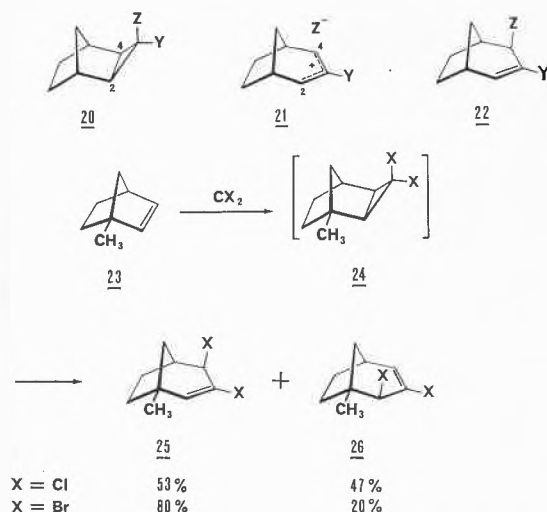
<sup>5</sup> C. W. JEFFORD, S. MAHAJAN, J. WASLYN and B. WAEGELL, *J. Amer. Chem. Soc.* **87** (1965) 2183.

<sup>6</sup> K. ALDER and R. REUBKE, *Chem. Ber.* **91** (1958) 1525.

<sup>7</sup> R. R. SAUERS and R. J. TUCKER, *J. Org. Chem.* **28** (1963) 876.

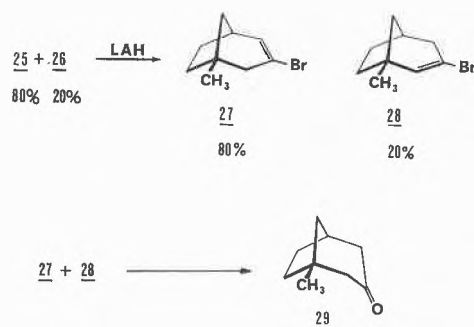
<sup>8</sup> C. W. JEFFORD, J. GUNSHER, D. T. HILL, P. BRUN, J. LEGRAS and B. WAEGELL, submitted to *Organic Syntheses*.

<sup>9</sup> a) C. W. JEFFORD, *Proc. Chem. Soc.* **1963**, 64; b) L. GHOSEZ and P. LAROCHE, *Proc. Chem. Soc.* **1963**, 90; c) R. C. DE SELMS and C. M. COMBS, *J. Org. Chem.* **28** (1963) 2206; d) E. BERGMANN, *J. Org. Chem.* **28** (1963) 2210.



The product compositions which are obtained from the reaction are also the same as the thermodynamic ratios; the different ratios for the chloro- and bromo-compounds could be ascribed to the steric interaction encountered by the bridgehead methyl group with the allylic halogen atom. Attempts to separate the isomers continually failed presumably because of their allylic isomerization<sup>5</sup>.

The reduction of the mixture of allylic isomers **25** and **26** with lithium aluminum hydride occurs with 100% allylic rearrangement, and as a further study using lithium aluminum deuteride shows, the S<sub>N</sub>2' process occurs such that the deuteride and bromide ions enter and leave on the *exo* face of **25** and **26**<sup>10</sup>.

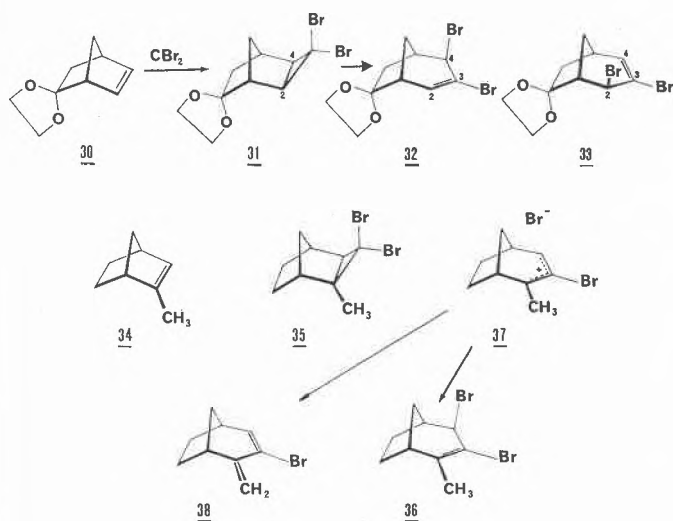


Hydrolysis of the mixture of vinyl bromides (**27** and **28**) gives a single product, viz., 1-methylbicyclo [3.2.1]octanone-3 (**29**). When the substituent on norbornene is some distance removed from the double bond, as in the ethyleneketal of norborn-2-en-5-one (**30**), then addition of dibromo- (and dichloro-) carbene results in the immediate formation of a 50 to 50 mixture of the *exo* isomers (**32** and **33**). Despite the apparent possibility of neighboring group participation, which would favor ionization, isomerization is relatively sluggish; so much so that the two isomers can be separated by fractional crystalli-

<sup>10</sup> C. W. JEFFORD, S. N. MAHAJAN and J. GUNSHER, *Tetrahedron* **24** (1968) 292.

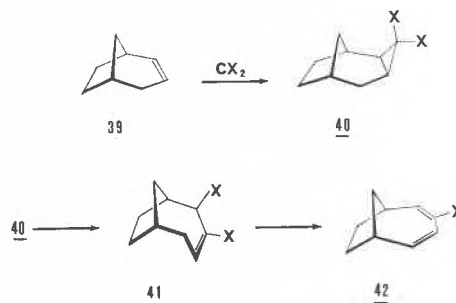
zation and identified the one from the other by n.m.r. analysis. Under ionizing conditions the thermodynamic equilibrium favors **32** over **33** by about 1 kilocalorie/mole. The difference in stability may spring from the fact that substituents on C-2 in **32** have a smaller space requirement than in **33** *vis-à-vis* the neighboring ketal grouping<sup>11</sup>.

There is no doubt that the bicyclo[3.2.1]octenyl cation (**21**) is easily formed, apart from the question of whether it arises during or after rearrangement of the cyclopropane adduct. The stability of the ion probably owes much to its rigidity which enables charge to be spread over all three atoms of the allyl portion in a way reminiscent of the cyclopropenyl cation<sup>12</sup>. Accordingly, the intermediacy of such a bicyclo[3.2.1]octenyl ion can provide a diversion to elimination or isomerization in appropriate cases. Thus, reaction of dibromocarbene with 2-methylnorbornene (**34**) gives the cyclopropane adduct (**35**) which can by-pass the rearranged product **36** by shedding a proton from the intermediate ion (**37**) to afford the conjugated diene (**38**)<sup>5</sup>.



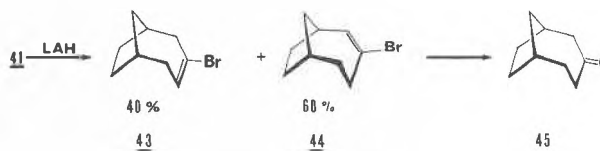
Bicyclo[3.2.1]octene-2 (**39**), which is isomeric with **9** and **34**, after carbene addition, should lose a proton in much the same way. However, its behavior is strikingly different. First of all, the adduct (**40**) is formed in greater yield (17 and 39% for the chloro- and bromo-derivatives respectively). Recent results indicate that the addition process is not stereospecific and the both *exo* and *endo* adducts are formed<sup>13</sup>. However the *exo* adduct (**40**) is preponderant. And secondly, it possesses remarkable thermal stability. Thus, propensity to rearrangement is not just a function of the cyclopropane ring, but rather

of the host cycle. However, by heating at 150°, either neat or in mesitylene, rearrangement can be brought about with formation of one product in high yield (80%), viz. *exo*-2,3-dibromobicyclo[4.2.1]nonene-3 (**41**). Thermodynamic control undoubtedly determines the course of such pyrolytic ring opening as only one of the two possible rearrangement products is observed.



Further heating of **41** in chlorobenzene expels hydrogen bromide with production of the diene **42**.

By using the same procedures as before, the *exo*-2,3-dibromobicyclo[4.2.1]nonene-3 (**41**) is converted into bicyclo[4.2.1]nonanone-3 (**45**)<sup>14, 4f</sup>.



However, reduction of (**41**) with lithium aluminum hydride occurs only with 60% allylic rearrangement. Clearly in the cycloheptenyl ring the stereoelectronic significance pertaining to the *quasi*-axial and *quasi*-equatorial bonds of the lower homologue has largely disappeared and simple S<sub>N</sub>2 displacement by hydride becomes competitive with the S<sub>N</sub>2' process<sup>14</sup>.

In all the cases of dihalocarbene addition to substituted norbornenes the addition is assumed to be *exo*. This assumption is based on the norbornene experiment and also on the stereochemistry of the rearranged products<sup>15</sup>. In contrast, norbornadiene (**46**) apparently undergoes both *exo* (**47**) and *endo* (**48**) addition. However, only the products of their presumed stereospecific rearrangement are found (**49** and **50**).

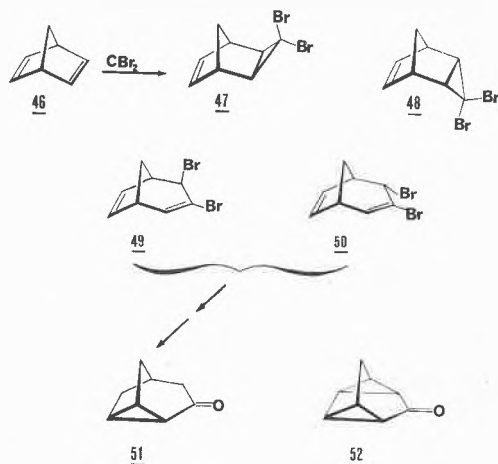
<sup>14</sup> Unpublished findings, C. W. JEFFORD and W. WOJNAROWSKI.

<sup>15</sup> The structures of all the compounds mentioned in this paper were rigorously established by detailed n.m.r. analyses making use of double resonance experiments (*cf.* refs. 4e and 15a-d); a) C. W. JEFFORD, B. WAEGELL and K. C. RAMEY, *J. Amer. Chem. Soc.* 87 (1965) 2191; b) C. W. JEFFORD, J. GUNSHER and K. C. RAMEY, *J. Amer. Chem. Soc.* 87 (1965) 4384; c) C. W. JEFFORD and K. C. RAMEY, *Tetrahedron* 24 (1968) 2927; d) B. WAEGELL and C. W. JEFFORD, p.105 in *Molecular Relaxation Processes*, Chemical Society Special Publication No 20, Academic Press, London and New York 1966.

<sup>11</sup> Unpublished findings, C. W. JEFFORD, B. WAEGELL, J. GORÉ, K. C. RAMEY and D. T. HILL.

<sup>12</sup> *Cf.* E. F. KIEFER and J. D. ROBERTS, *J. Amer. Chem. Soc.* 84 (1962) 784.

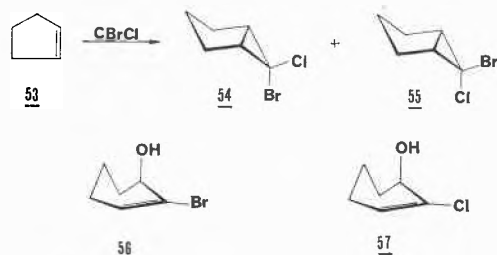
<sup>13</sup> Unpublished findings, C. W. JEFFORD and F. DELAY (*cf.* P. CRABBÉ, *Industrie Belg.* 34 (1969) 15).



The reduction of **49** and **50**, followed by hydrolysis, affords the tricyclic ketone **51**<sup>16</sup>. In a similar way, starting from **46**, the tetracyclic ketone **52** is prepared<sup>17</sup>. This same route has been used for the synthesis of the mechanistically interesting benzobicyclo[3.2.1]octene-2 skeleton<sup>18, 19</sup>.

#### Monohalocarbenes and Bridged Bicyclic Olefins

An early experiment suggested that only one of the geminal cyclopropyl halogens underwent migration on rearrangement. The interaction of bromochlorocarbene and cyclopentene (**53**) gave two isomeric adducts (**54** and **55**); it was noticed that each isomer on separate treatment with aqueous silver ion gave the allylic alcohols (**56** and **57**) with the important distinction that one of them lost chlorine and the other bromine. However, which adduct gave which alcohol was not ascertained<sup>20 a</sup>. A similar result was reported with indene<sup>20 b</sup>.



<sup>16</sup> W. R. MOORE, W. R. MOSER and J. E. LAPRADE, *J. Org. Chem.* 28 (1963) 2200.

<sup>17</sup> N. A. LEBEL and R. N. LIESEMER, *J. Amer. Chem. Soc.* 87 (1965) 4301.

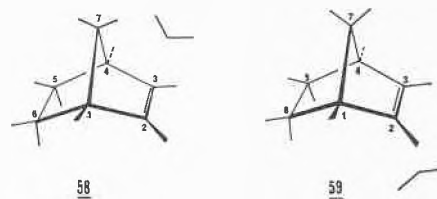
<sup>18</sup> a) Although details of the stereochemistry were not reported, dichlorocarbene undergoes addition to 2,3-benzonorbornadiene with formation of axial-2,3-dichlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-diene (see refs 19a) and 19b); b) For the addition of dichlorocarbene to dibenzobicyclo[2.2.2]octatriene see S. J. CRISTOL, R. M. SECUEIRA and G. O. MAYO, *J. Amer. Chem. Soc.* 90 (1968) 5564.

<sup>19</sup> a) H. TANIDA, K. TORI and K. KITAHONOKI, *J. Amer. Chem. Soc.* 89 (1967) 3212; b) J. W. ROSENTHAL and S. WINSTEIN, *Tetrahedron Letters* 1970, 2683; c) J. M. BROWN and E. N. CAIN, *J. Amer. Chem. Soc.* 92 (1970) 3821.

<sup>20</sup> a) P. S. SKELL and P. SANDLER, *J. Amer. Chem. Soc.* 80 (1958) 2124; b) W. E. PARHAM and R. R. TWELVES, *J. Org. Chem.* 22 (1951) 730.

It can be appreciated that a nice way to examine some of these questions is to employ a substituted carbene where only one of the substituents can act as a leaving group. For norbornene-like olefins there will be four possible addition modes, *exo-syn*, *exo-anti*, *endo-syn* and *endo-anti*, and consequently, a correlation should obtain between stereochemistry of rearrangement with orientation of leaving group. Accordingly, the addition of monohalocarbene to bicyclo[2.2.2]octene-2 (**9**), norbornene (**16**) and its 1-methyl (**23**) and 2-methyl (**34**) derivatives was undertaken. Chlorocarbene, or rather dichloromethyl lithium<sup>21 b</sup>, was prepared from the interaction of methyl lithium and methylene chloride and allowed to react *in situ* with the olefin<sup>21</sup>. In all cases addition took place in the *syn* and *anti* senses and for the norbornenes only on the *exo* side<sup>22, 23</sup>.

Exclusive *exo*-cyclopropanation has been ascribed to the subtle distinction which torsional interactions can make between the transition states for *exo* and *endo* addition (**58** and **59**)<sup>24</sup>.



It has been proposed that in **58**, as bonding increases, eclipsing between the Cl-H and C2-H bonds and between the C3-H and C4-H bonds is relieved, whereas it is worsened in **59**. However, this argument is not entirely persuasive because it should apply with equal rigor to norbornadiene which enjoys the same geometry about carbons 1, 2, 3 and 4. Experiment shows that norbornadiene undergoes some *endo* addition<sup>25</sup>, which suggests that the absence of the *endo* C5, C6 protons or the appearance of the second double bond are responsible in some way for the difference in behavior.

Although a stereoelectronic factor should not be discounted to account for the behavior of norbornene, steric approach control could be important. If the incipient bond between C2-C3 and the carbenic carbon is long, then the presence or absence of *endo* hydrogen atoms on C5-C6 will constitute the determinative difference between the *exo* and *endo* transition states (**58** and **59**).

<sup>21</sup> a) Cf. G. L. CLOSS and L. E. CLOSS, *J. Amer. Chem. Soc.* 82 (1963) 5723; b) G. KÖBRICH, *Angew. Chem.* (intern. edition) 9 (1970) 169.

<sup>22</sup> C. W. JEFFORD and R. T. MEDARY, *Tetrahedron* 23 (1967) 4123.

<sup>23</sup> C. W. JEFFORD and W. WOJNAROWSKI, *Tetrahedron Letters* No 2 (1968) 193, 199.

<sup>24</sup> P. V. R. SCHLEYER, *J. Amer. Chem. Soc.* 89 (1967) 699, 701.

<sup>25</sup> a) R. R. SAUERS and P. E. SONNET, *Tetrahedron* 20 (1964) 1029; b) H. E. SIMMONS, E. P. BLANCHARD and R. D. SMITH, *J. Amer. Chem. Soc.* 86 (1964) 1347; (Methylene transfer to norbornadiene gives *exo* and *endo*-monoadducts in a 6 to 1 ratio).

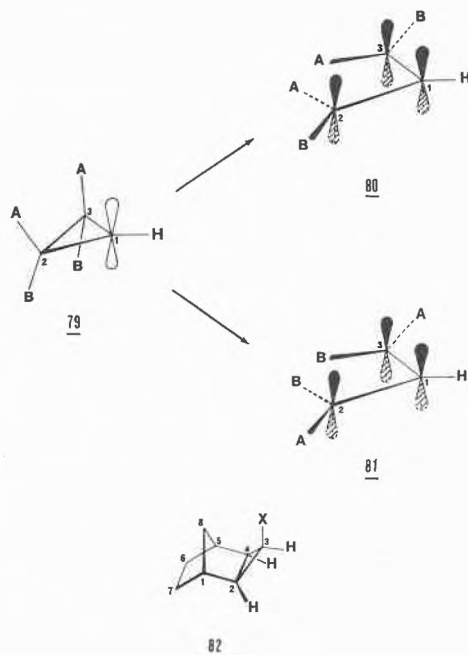


unscathed after exposure to heat (e.g. 180° for 24 hours) or on treatment with silver ion in aqueous-acetone.

The same pattern of addition and rearrangement is experienced when fluorobromocarbene is used. The action of potassium *t*-butoxide on dibromofluoromethane in the presence of norbornene gives *exo*-3,3-*anti*-bromo-*syn*-fluorotricyclo [3.2.1.0<sup>2,4</sup>]octane (**76**) and *exo*-4-bromo-3-fluorobicyclo [3.2.1]octene-2 (**78**) in a ratio of 1 : 1.3. Thus a *syn*-disposed carbon-bromine bond in the presumed adduct **77** has broken, whereas, as expected, a *syn*-carbon-fluorine bond (as in **76**) held firm. The product ratio nicely illustrates that sheer bulk as such does not count in the transition states for *syn* and *anti* addition, but rather that dispersion forces and hence polarizability do<sup>30</sup>. Analogous findings have been reported for the addition of fluorochlorocarbene to norbornene and for the stereochemistry of rearrangement of *exo*-*syn* and *exo*-*anti*-3-chloro-8-oxatricyclo [3.2.1.0<sup>2,4</sup>]octane<sup>31</sup>.

### Rearrangement Process

It is immediately obvious from the thermal behavior of the cyclopropane adducts that it is the orientation of the cyclopropyl leaving group which determines uniquely whether the ring will open or not. It is now known that the stereochemistry of such cyclopropyl-allylic transformations is governed by the principle of the conservation of orbital symmetry. For the hypothetical case of the conversion of a cyclopropyl to an allylic cation, the symmetry of the highest occupied molecular orbital of the derived allylic ion dictates that rupture

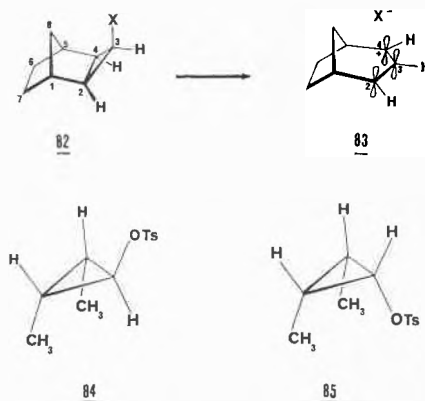


<sup>30</sup> C. W. JEFFORD and D. T. HILL, *Tetrahedron Letters* 1969, 1957.

<sup>31</sup> a) L. GHOSEZ, G. SLINCKX, M. GLINEUR, P. HOET and P. LAROCHE, *Tetrahedron Letters* No 29 (1967) 2773; b) L. GHOSEZ, P. LAROCHE and G. SLINCKX, *Tetrahedron Letters* No 29 (1967) 2767.

of the carbon-carbon bond opposite the cationic center (on C-1 in **79**) occurs with a disrotatory prising apart of the constituent atomic orbitals<sup>32</sup>. Two such modes are possible (**79** → **80**) and **79** → **81**).

However, for the tri cyclic cyclopropane adducts under discussion only *one* disrotatory mode is mechanically feasible as the other is forbidden by the constraint imposed by the cyclopentane ring. In short, rupture of the C2-C4 bond can only occur by C3 moving in the *endo* direction with a concomitant disrotatory splaying apart of the hydrogen atoms on C2 and C4. Thus the C4-C5 and C2-C1 bonds of **82** correspond to the bonds labelled A in **79**.



Moreover, considerable driving force for this process is provided by the strain released on collapse of the regular boat geometry constituted by atoms C1-C5 and C8 in **82**. As the present findings reveal, such rearrangement only occurs when the leaving group at C-3 is *syn*-disposed. A conclusion which may be drawn is that only the *syn*-disposed bond is ionizable and that as soon as a positive charge is created at C-3 it is immediately dispersed to C-2 and C-4 by the device of disrotatory rupture of the C2-C4 bond. Therefore, on the principle of least motion<sup>33</sup>, an allylic cation and its anionic companion will be created in close contact (**83**). From there, migration of the anion to C-2 or C-4 on the *exo* side is but a short step. Several examples substantiate the stereoelectronic requirement of this presumed ionic rearrangement. Indeed, in the actual event of trying to generate a cyclopropyl cation by solvolysis, kinetic evidence has demonstrated that ionization proceeds at the same pace as ring opening with restriction to one disrotatory mode<sup>34,35</sup>: (e.g. **84** solvolyses many times faster than **85**).

<sup>32</sup> R. B. WOODWARD and R. HOFFMANN, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim (Bergstraße) 1970.

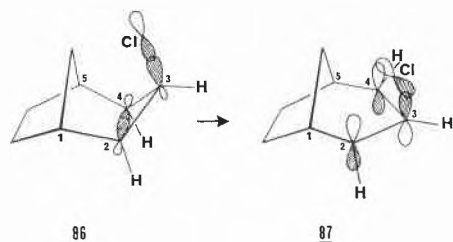
<sup>33</sup> O. S. TEE, *J. Amer. Chem. Soc.* 91 (1969) 7144.

<sup>34</sup> For examples of the solvolysis of cyclopropyl derivatives see P. v. R. SCHLEYER, G. W. VAN DINE, U. SCHÖLLKOPF and J. Paust, *J. Amer. Chem. Soc.* 88 (1966) 2869 and refs. cited therein; also U. SCHÖLLKOPF, K. FELLENBERGER, M. PATSCH, P. v. R. SCHLEYER, T. SU and G. W. VAN DINE, *Tetrahedron Letters* No 37 (1967) 3639. For a review see U. SCHÖLLKOPF, *Angew. Chem.* 80 (1968) 603.

<sup>35</sup> a) W. E. PARHAM and K. S. YONG, *J. Org. Chem.* 35 (1970) 683; b) M. S. BAIRD and C. B. REESE, *Tetrahedron Letters* 1969, 2117.

However, another, more subtle description is conceivable. If the migrating halogen atom makes use of *both* lobes of its atomic orbital, then the cyclopropylallyl transposition can be effected in a fully concerted manner by a suprafacial [1,3] sigmatropic shift<sup>32, 36</sup>. As four electrons are involved in the rearrangement process, the transition state requires that the basis set of atomic orbitals possess MÖBIUS topology<sup>37</sup>. Such a basis set is appropriately constructed by the disrotatory breakage of the C2-C4 bond and by migration of the leaving group so that both lobes of its *p*-orbital span the developing atomic orbitals on C-3 and C-4 (or on C-3 and C-2) (**86** → **87**). The resulting array of atomic orbitals has only one non-trivial sign inversion between C-2 and C-3. This description is at once simple and satisfactory in that covalent bonding is continuously maintained in the rearrangement process.

Unfortunately, the present results do not permit an unambiguous distinction between these alternatives; a similar difficulty arises for the isomerization of allylic halides where migration of anion occurs across the *exo*



face (e.g. **25** → **26** and **33** → **32**). Both an ionic dissociation-recombination process as well as a suprafacial [1,3] sigmatropic shift can be envisaged.

### Conclusion

Two novel features emerge from the present investigations. Firstly, from the view-point of preparative utility, the reaction of dihalocarbenes to bridged bicyclic olefins furnishes a simple means of adding an extra carbon without profoundly disturbing the original skeleton, thereby providing a neat entry to the less accessible higher homologues.

The second, and a somewhat unexpected, result is that, despite the number and diversity of studies which have been devoted to norbornene over the years, an entirely new facet of its chemistry has been uncovered. Thus dispersion forces exercise control over the addition of monohalocarbenes and once the cyclopropane is formed, geometric strictures on bond movement and the subtle demands made by orbital symmetry combine to produce an all or none effect in which the adduct either undergoes facile stereospecific rearrangement or holds fast. Nevertheless, there remains in these apparently restricted processes a degree of latitude, the limits of which need to be tested and defined by means of appropriately designed experiments.

### Acknowledgements

I am grateful to the National Science Foundation and the Petroleum Research Fund (administered by the American Chemical Society) for the provision of funds which were indispensable for the realization of much of this work. Last, but not least, I wish to acknowledge the skill and contributions of my co-workers whose names are cited in the references.

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