Notes A department for short papers of immediate interest.

Stability and Ease of Formation of Endo and Exo Double Bonds in 5- and 6-Ring Systems

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In 1954, Brown and coworkers proposed that "reactions will proceed in such a manner as to favor the formation or retention of an exo double bond in the 5-ring and to avoid the formation or retention of the exo double bond in the 6-ring systems."[1] By means of this generalization, it was possible to correlate a vast amount of data on 5- and 6-ring systems available at the time, and it has been invoked several times in the subsequent literature.[2]

However, an examination of the approximations and postulates on which the generalization is based reveals a severe limitation on the part that concerns exo double bond formation or retention in 5-ring systems. The generalization is based on a comparison of exo double bonds in 5-rings with exo double bonds in 6-rings[3] and *does not apply to a comparison between endo and exo double bonds in 5-rings.*

For example, the dehydration of 1-alkylcyclopentanols yields 1-alkylcyclopentenes,[4] a reaction which does *not* proceed in such a manner as to favor the formation of an exo double bond in the 5-ring system. Similarly, the isomerization of alkylidenecyclopentanes to 1-alkylcyclopentenes,[1] such as isopropylidenecyclopentane to 1-isopropylcyclopentene,[5] does *not* favor the retention of an exo double bond in the 5-ring system.

Taken from its context, the sweeping terms of the generalization have led to its erroneous use in comparing the stability[2a,b,c] and ease of formation[2a,d] of endo and exo double bonds in 5-rings.

Since theory and experiment agree that an exo double bond in the 6-ring system is unstable compared to an endo double bond in the 6-ring or to an exo double bond in the 5-ring system,[1] the generalization that *reactions will proceed in such a manner as to avoid the formation or retention of an exo double bond in a 6-ring system* is sufficient to correlate most[6] of the existing data[1,2a] and avoids the ambiguous case of exo *vs.* endo double bonds in 5-ring systems.[2b,c,d]

As far as the available experimental data are concerned, it seems that ordinarily an endo double bond in the 5-ring is at least as stable as an exo double bond in the 5-ring system.[4,5]

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(1) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

(2) (a) O. H. Wheeler, *Chemistry & Industry*, 900, 1020 (1954). (b) O. H. Wheeler and I. Lerner, *J. Am. Chem. Soc.*, **78**, 63 (1956). (c) O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 3216 (1956). (d) A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **78**, 1216 (1956).

(3) Reference (1) does not make it clear that this condition, imposed on the argument, carries over into the generalization. Reference (2a) explicitly abandons the restriction.

(4) R. A. Raphael, *Chemistry of Carbon Compounds*, E. H. Rodd, editor, Elsevier Publishing Co., Houston, 1953, vol. IIA, pp. 78, 79, 87.

(5) O. Wallach, *Ann.*, **353**, 307 (1907). *Cf.* H. J. Schaeffer and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 128 (1956) for the isomerization of benzalcyclopentane to 1-benzylcyclopentene.

(6) Some interesting cases in which an endo double bond in a 6-ring system shifts to the exo position have been observed (a) during Wolff-Kishner reductions; G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **32**, 1817 (1949); (b) in the rearrangement of 1-cyclohexenylmethyl diphenylacetate to 2-methylenecyclohexyldiphenylacetic acid; R. T. Arnold and W. W. Lee, *J. Am. Chem. Soc.*, **75**, 5396 (1953); (c) in the allylic rearrangement of 1-cyclohexenylcarbinol to 2-methylenecyclohexanol; reference (2d).

Generalization Dealing with Chemical Behavior of 5- and 6-Membered Ring Compounds

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In a paper published in 1954, an attempt was made to rationalize the chemical behavior of five- and six-membered ring compounds.[1] It was pointed out that reactions involving a change in coordination number of a ring atom from four to three proceed relatively rapidly in cyclopentane derivatives and relatively slowly in cyclohexane derivatives. Conversely, reactions involving a change in coordination number from three to four proceed slowly in 5- and rapidly in 6-rings.

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(1) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).