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

B. Raymond Fleck

Received July 25, 1956

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]

Department of Chemistry
St. Edward's University
Austin 4, Tex.

---

[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

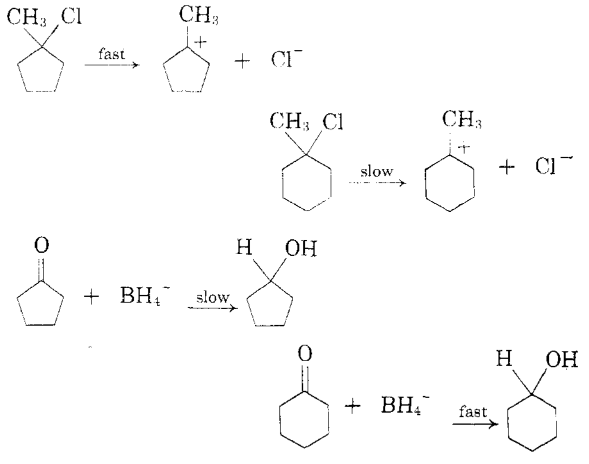
Herbert C. Brown

Received February 1, 1957

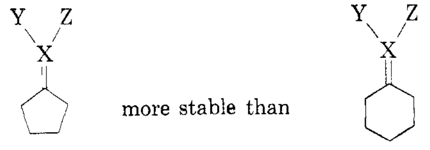
In a paper published in 1954, an attempt was made to rationalize the chemical behavior of five- and six-membered ring compounds.[1] It was pointed out that reactions involving a change in coordination number of a ring atom from four to three proceed relatively rapidly in cyclopentane derivatives and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

---

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

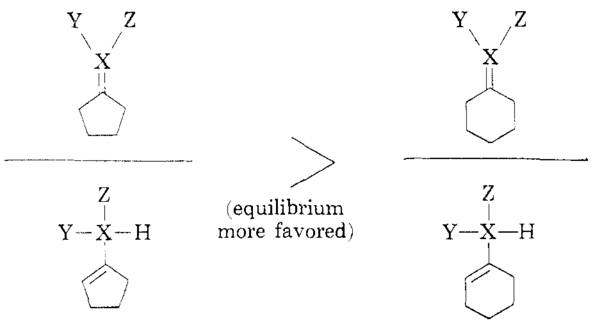


These results suggest that in the 5-membered ring a trigonal structure for one of the ring atoms is strongly favored over the tetrahedral arrangement, whereas the reverse is true in the 6-membered ring. It was therefore proposed that an exo double bond in all 5-membered ring systems will be more stable toward changes involving loss of the exocyclic double bond than will the corresponding exo double bond in 6-ring systems.



This proposal was supported by the higher heat of hydrogenation of cyclohexanone as compared to cyclopentanone. Also, many compounds which can react to form rings yield 6-ring derivatives preferentially, if there is no exocyclic double bond, but form the 5-ring compound preferentially when an exo double bond is present.

Endo double bonds in 5- and 6-rings differ in stability. However, in numerous cases the available data indicate that the difference in stability is smaller than that observed in the corresponding exo bonds. In such cases, the relative stability of the latter should be the controlling factor in the relative effects of 5- and 6-rings on exo-endo equilibria. Therefore, we can write for the equilibrium ratios of exo-endo isomeric pairs:



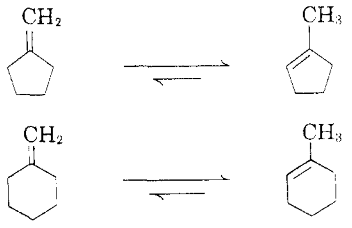
On the basis of these considerations, the following generalization was proposed: reactions will proceed in such a manner as to favor the formation or retention of an exo double bond in the 5-ring [relative to the corresponding reaction in the 6-ring] and to avoid the formation or retention of the exo double bond in the 6-ring [relative to the related 5-ring] system.

The generalization was discussed in detail in the paper and was applied to the rationalization of a large number of phenomena in the chemistry of 5- and 6-membered ring systems.

In striving for conciseness the two qualifying statements [in brackets] were eliminated.[2] In view of the fact that the entire discussion leading up to the generalization dealt with the marked difference in reactivity of double bonds exo to 5- and 6-ring systems, the bracketed statements appeared redundant and unnecessary. Utilized in the light of our discussion, no difficulty need have arisen. However, taken out of context, the generalization can be misleading, and it has been misinterpreted.[3]

For example, in a recent Communication[4] the prediction that methylenecyclopentane should be more stable than 1-methylcyclopentene is ascribed to the generalization. Likewise, Weinstock, Pearson, and Bordwell have stated, ". . .Brown, Brewster, and Shechter. . . have emphasied the greater stability of an endo over an exo double bond in the cyclohexane series and the reverse in the cyclopentane series."[5]

It is unfortunate that misinterpretations have arisen. In the first sentence of the paragraph immediately following the generalization it is stated, "In the simple hydrocarbons, endocyclic are far more stable than exocyclic double bonds."[1] In other words, both methylenecyclopentane and methylenecyclohexane are unstable relative to the isomeric 1-methylcyclopentene and 1-methylcyclohexene.



On the other hand, in the cyclic ketones the op-

---

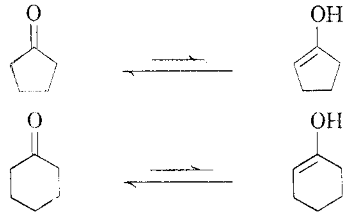
[2] The present author wishes to take sole responsibility for this omission.

[3] See discussion of this point by R. Fleck, *J. Org. Chem.*, **22**, 439 (1957).

[4] R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **79**, 253 (1957). The data reported on the heats of hydrogenation of methylenecyclopentane, 1-methylcyclopentene, methylenecyclohexane and 1-methylcyclohexene are exceedingly interesting and quite valuable in providing a rigorous test of the scope of the proposed generalization. However, it would be inappropriate to examine their implication prior to discussion and interpretation by the authors.

[5] J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Am. Chem. Soc.*, **78**, 3468 (1956).

posite is true. In these compounds the preferred form is the exo double bond structures.



It is therefore clear that no simple generalization can hope to predict the relative stabilities of exo *versus* endo double bonds *within any single ring system.*[6] The original generalization was not intended to handle such problems.

The generalization does predict that both the rate and the equilibrium for the reaction of a nucleophilic reagent, such as cyanide ion, should be favored for cyclohexanone as compared to cyclopentanone. It likewise predicts that the amount of enol present in the ketone at equilibrium should be greater for cyclohexanone as compared to cyclopentanone. Both predictions are supported by the available experimental data.

The following revised generalization is offered in the hope that it may avoid some of the misunderstandings which have resulted from the version in its original form.

Double bonds which are exo to a 5-ring are less reactive and more stable (relative to the saturated derivatives) than related double bonds which are exo to a 6-ring. Reactions which involve the formation or retention of an exo double bond in a 5-ring derivative will be favored over corresponding reactions which involve the formation or retention of an exo double bond in a 6-ring derivative. Reactions which involve the loss of an exo double bond will be favored in the 6-ring as compared to the corresponding 5-ring derivative.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, IND.

---

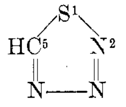
(6) On this basis Brother Fleck's suggestion that "reactions will proceed in such a manner as to avoid the formation or retention of an exo double bond in a 6-ring system" cannot be applied generally since it would predict the preferred existence of cyclohexanone in the enol form.

Infrared Spectrum of the So-called 5-Amino-1,2,3,4-thiatriazole

EUGENE LIEBER, EDWIN OFTEDAHL, C. N. PILLAI, AND RALPH D. HITES

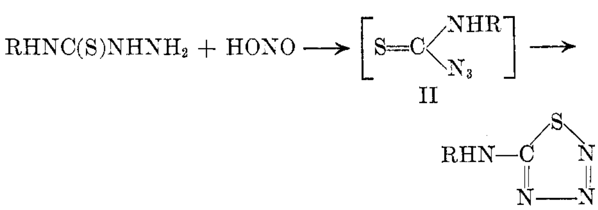
Received September 10, 1956

The so-called 1,2,3,4-thiatriazole ring,[1] I, has



I

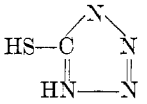
received practically no attention in the literature since Freund and Schander,[2] in 1896, reported on the basis of degradative evidence, that the product of the reaction of one mole of nitrous acid with thiosemicarbazide had the structure now designated as 5-amino-1,2,3,4-thiatriazole, III:



II

III
R = H

While the data presented[2] clearly exclude the isomeric tetrazole structure, IV, it is not as unequivocal in differentiating the acyclic thiocarbamyl azide, II, and the isomeric thiatriazole ring, III.



IV

On evidence also not unequivocal, Olivari-Mandala[3] suggested that the product of Freund and Schander,[2] III, was identical to the reaction products of isothiocyanates with hydrazoic acid to which he gave the structure II:

$$RNCS + HN_3 \longrightarrow II$$

The only additional work which contributes to the structure of the thiosemicarbazide–nitrous acid reaction product is by Sahasrabudhey and Krall[4] in 1941. A gasometric study revealed that thiosemicarbazide absorbs one molar proportion of nitrous acid in the presence of N-hydrochloric acid, without gas evolution. They accepted structure III without further evidence.

The two key features upon which Freund and Schander[2] based their selection of III were: (1) its decomposition in aqueous solution with precipitation of sulfur and evolution of nitrogen (or at least of a gas identified merely as inert) and (2) the lack of hydrazoic acid among the degradation products. This latter point, however, can be refuted from the experimental data of Freund and Schander,[2] since in one of their experiments on treatment of III (or II[?]) with aqueous sodium hydroxide and subsequent acidification, they reported "an odor of hydrazoic acid," unfortunately

---

(1) Nomenclature and ring number system from A. M. Patterson and L. T. Capell, *The Ring Index,* Reinhold Publishing Corp., New York, 1940.

(2) M. Freund and A. Schander, *Ber.,* **29,** 2500 (1896).

(3) E. Olivari-Mandala, *Gazz. chim. ital.,* **44** (1), 670 (1914).

(4) Sahasrabudhey and Krall, *J. Indian Chem. Soc.,* **13,** 226 (1941).