Tetrahedron Letters No. 48, pp 4189 - 4192, 1974. Pergamon Press. Printed in Great Britain.

A ONE-STEP CONVERSION OF BASKETANE TO TWISTANE. CATALYTIC HYDROGENOLYSIS OF CYCLOBUTANE RINGS IN STRAINED POLYCYCLIC HYDROCARBONS

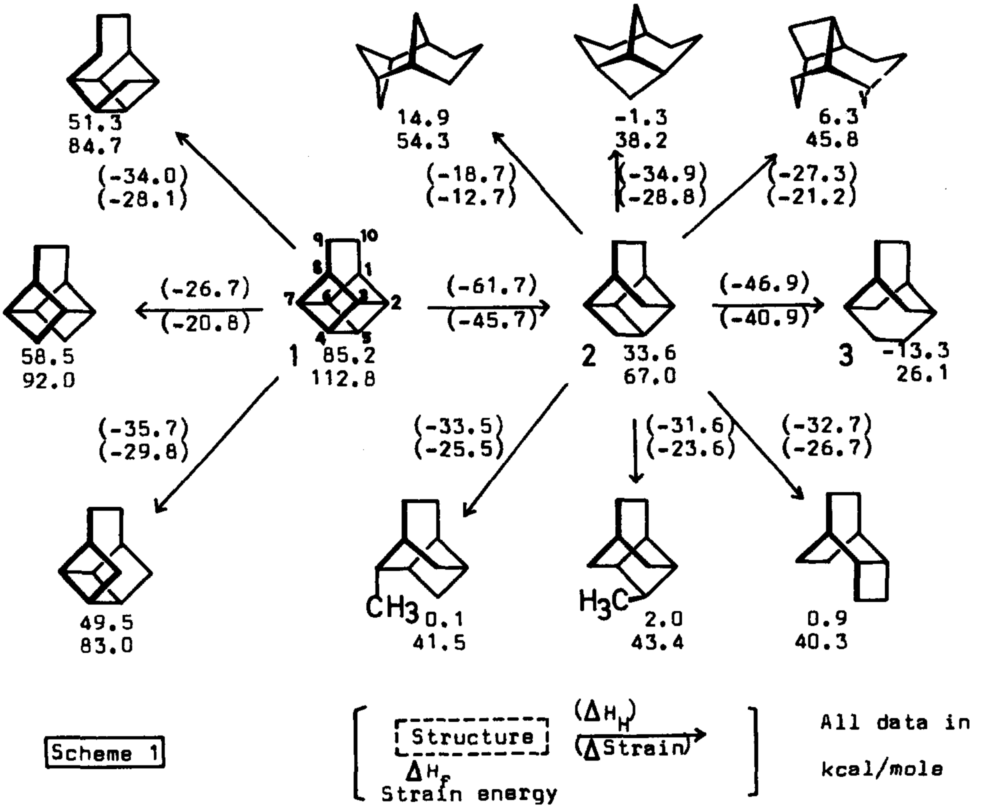
Eiji Ōsawa*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo
060 JAPAN
Paul von R. Schleyer*, Lawrence W. K. Chang and Vinayak V. Kane
Department of Chemistry, Princeton University, Princeton, New Jersey 08540 USA

(Received in UK 26 September 1974; accepted for publication 17 October 1974)

Recent work on the catalytic hydrogenation of basketane (1)[1] prompts us to report our results and interpretations. Sasaki, Zunker and Musso[1a] demonstrated that the C3-C4 bond of 1 is cleaved (not the C4-C5 bond as suggested by Masamune)[2], resulting in an unsymmetrical structure (2) for dihydrobasketane. Masamune[2] noted that his sample of dihydrobasketane was "slightly contaminated with tetrahydrobasketane as evidenced by its mass spectrum." Since 2 contains a bicyclo[2.2.0]hexane unit known to undergo ready hydrogenolysis,[3] we expected that further hydrogenation of 2 should cleave the C5-C6 bond and give twistane(3).

Hydrogenation of basketane (1)[4,5] over 5 % Pd/C in hexane-methanol using a Parr apparatus with an initial hydrogen pressure of 3.3 atm at room temperature for one night gave waxy product in 70 % yield after sublimation. Glc analysis revealed a predominant component (70 %) contaminated with at least three minor components (10, 8 and 12 % in increasing order of glc retention time on Carbowax 20M). Although we have not fully characterized the minor products, the major component, mp 160-162° (separated by glc on 10 % FFAP), was identical in every respect with twistane (3).[1b,6] Since basketane is not readily accessible,[4,5] the present twistane synthesis does not provide any advantage over the known methods.[6] Nevertheless, the remarkably high selectivity of this and related single bond hydrogenolyses deserves further discussion.

Musso[1] suggested the importance of C-C bond lengths as a criterion for

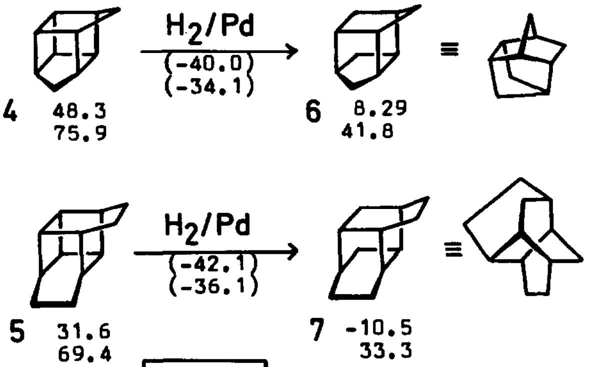


Scheme 1

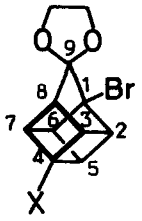
determining which bond should undergo hydrogenolysis. For example, the basketane C3-C4 bond (1.55 Å) is significantly longer than the C4-C5 bond (1.52 Å), and thus should be more strained and more reactive. However, if the product-determining step involves a transition state closer to product than to initial state, then the relative thermodynamic stabilities of the possible products, rather than the distribution of strain in the initial state, should govern the course of reaction.

Scheme 1 summarizes calculated[7] heats of formation ($\Delta H_f^{25^\circ}$) and strain energies of all possible structures resulting from hydrogenolyses of each type of cyclobutane bond in basketane (1) and in dihydrobasketane (2). The difference in ΔH_f between starting material and hydrogenated product gives the heat of hydrogenation (ΔH_H) and affords a measure of relative ease of reaction. The differences in strain energies (ΔStrain) can be compared similarly. From 2, both ΔH_H and ΔStrain for the reaction leading to twistane (3) is by far the largest among the seven possibilities of ring opening. Likewise, 2 is the most stable isomer which can be produced from 1. Thus, the results of calculation and experiment are in good agreement.

Recently, Hirao and his group[8] found additional examples of selective catalytic hydrogenolysis of related strained cage hydrocarbons: 1,3-homocubane (4) and pentacyclo[$6.4.0.0^{2,5}.0^{3,12}.0^{4,9}$]dodecane (5) give only tetracyclo[$5.2.1.0^{2,6}.0^{4,8}$]decane (6)[9] and [8]ditwistane (7)[10], respectively (Scheme 2). In order to study the thermodynamic stability of 6, a small sample was treated with seven times its weight of anhydrous aluminum bromide in carbon disulfide under reflux for 20 hours. No significant change occurred as judged by glc analysis of the reaction mixture. Further heating under nitrogen at 100° C for 1.5 hour in a glass pressure bottle resulted in complete decomposition of 6, giving a dark coloured residue, from which the disproportionation product, adamantane, was detected by glc. From these results, we conclude that 6 is the most stable isomer among the $C_{10}H_{14}$ hydrocarbons, and this is indicated by force field calculations as well. Therefore, the hydrogenolysis of 4 also proceeds to relieve the largest amount of strain; 7 should be more stable than any other possible products from 5.



Scheme 2



8

Ring opening reactions other than hydrogenolysis also proceed by thermodynamic control. Klunder and Zwanenberg[11] showed that the first ring opening step of a homocubane system (8) undergoing homoallylic ($X = \overset{-}{C}HCN$)[11a] or Wagner-Meerwein rearrangements ($X = \overset{+}{C}H_2$)[11b] invariably involve the cleavage of the C3-C4 bonds.

Calculation of ΔH_H and ΔStrain for all the possible C-C bond cleavage reactions of homocubane itself confirm that opening of the C3-C4 bond should be much more favorable than the alternatives.

Since the central bond of bicyc[2.2.0]hexane is known to be extraordinarily long,[12] those bonds of 2, 4 and 5 which cleaved upon hydrogenolysis are very likely to be the longest bonds in these molecules. Thus, the two methods of prediction have so far found the same answers. However, there may be cases where they do not agree, and experimental tests should reveal which factor is more important.

Acknowledgments. We are grateful to Prof. H. Musso for discussion and preprints. Thanks are also due to Professors P. Deslongchamps, O. Yonemitsu, K. Hirao, R. R. Sauers, S. Masamune and T. Wipke for their advice and help. This work was supported at Princeton by grants from the National Institute of Health and Hoffmann-La Roche, Inc., Nutley, N. J.

REFERENCES AND NOTES

(1) (a) N. A. Sasaki, R. Zunker and H. Musso, Chem. Ber., 106, 2992 (1973); (b) Prof. Musso has also studied the exhaustive hydrogenation of basketane independently and identified three of the products; Chem. Ber., in press.

(2) S. Masamune, H. Cuts and M. G. Hogben, Tetradedron Lett., 1017 (1966).

(3) E. E. van Tamelen and D. Cartz, J. Amer. Chem. Soc., 93, 6102 (1971).

(4) H. G. Cuts, E. N. Cain, H. Westberg and S. Masamune in "Org. Photochem. Synth.", ed. R. Srinivasan, John Wiley & Sons, Inc., N. Y. 1971, p. 83.

(5) W. G. Dauben, C. H. Schallhorn and D. L. Whalen, J. Amer. Chem. Soc., 93, 1446 (1971).

(6) (a) H. W. Whilock, Jr. and M. W. Siefken, ibid., 90, 4929 (1968); (b) A. Belanger, J. Poupart and P. Deslongchamps, Tetrahedron Lett., 2127 (1968); (c) K. Adachi, K. Naemura and M. Nakazaki, ibid., 5467 (1968); (d) M. Tichy and J. Sicher, Coll. Czech. Chem. Commun., 37, 3106 (1972).

(7) E. M. Engler, J. D. Andose and P. von R. Schleyer, J. Amer. Chem. Soc., 95, 8005 (1973). Only those results obtained with the Engler force field are presented here; the 1971 Allinger force field gives almost the same results.

(8) K. Hirao, T. Iwakuma, M. Taniguchi, E. Abe, O. Yonemitsu, T. Date and K. Kotera, Chem. Commun., 691 (1974).

(9) Cf. (a) T. R. Henderson, Dissertation Abstracts, 1939-B (1973); (b) I. Rothberg, J. Fraser, R. Garnick, J. C. King, S. Kirsch and H. Skidanow, J. Org. Chem., 39, 870 (1974).

(10) For nomenclature see W. D. Graham, P. v. R. Schleyer, E. W. Hagaman and E. Wenkert, J. Amer. Chem. Soc., 95, 5785 (1973). Eight carbons are in common between two twistane units.

(11) A. J. H. Klunder and B. Zwanenburg (a) Tetrahedron Lett., 2383 (1972); (b) Tetrahedron, 29, 161 (1973).

(12) B. Andersen and R. Srinivasan, Acta Chem. Scand., 26, 3468 (1972).