CHEMISTRY LETTERS, pp. 1203-1204, 1975. Published by the Chemical Society of Japan

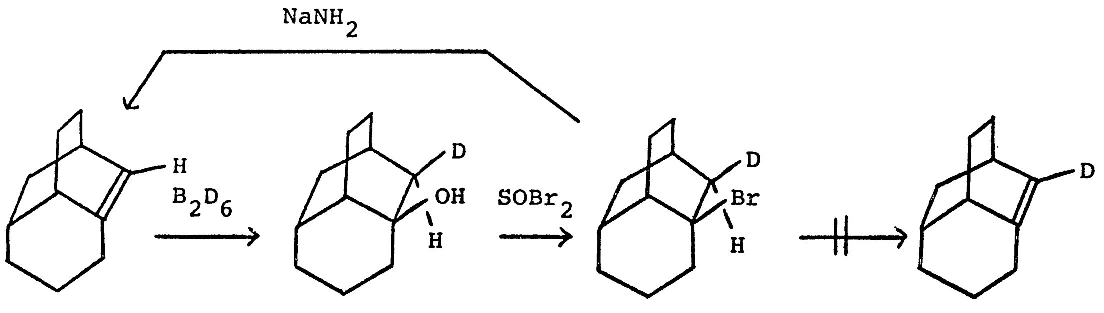
AN EXPERIMENTAL EVIDENCE FOR *CIS* ELIMINATION MECHANISM IN THE FORMATION OF A BREDT COMPOUND

Yoshiaki FUJIKURA, Yoshiaki INAMOTO,* Naotake TAKAISHI,
Hiroshi IKEDA, and Koji AIGAMI
Industrial Research Laboratories, Kao Soap Co., Ltd., Wakayama 640-91

Dehydrobromination of 3-bromotricyclo[5.3.1.$0^{3,8}$]undecane-2-*exo*-*d* (**3d**) gave almost exclusively the undeuterated Bredt olefin, demonstrating unequivocally a *cis* elimination mechanism.

In a series of study on Bredt compound, Wiseman and his colleagues[1] found a predominant formation of the less stable bicyclo[4.2.1]non-1(8)-ene in the pyrolysis of bicyclo[4.2.1]non-1-yltrimethylammonium hydroxide. The result was successfully interpreted in terms of kinetic control in the Hofmann reaction, assuming a *cis* elimination mechanism where the 8-*exo*-hydrogen, held rigidly *cis* to the leaving ammonium group, was preferably eliminated over the conformationally more mobile 2-*exo*-hydrogen. Our result[2a] on a ready formation of 4-homoisotwist-2-ene (tricyclo[5.3.1.$0^{3,8}$]undec-2-ene) (**1**) in dehydrobromination of 3-bromo-4-homoisotwistane (**3**)[2b] was explained well with this postulation. Although White and Kim[3] took their result on the formation of bicyclo[3.3.1]non-1-ene only from *cis* isomer of *N*-sulfoxyiminooxazoline-fused bicyclo[3.3.1]nonane as an evidence for the Wiseman's postulate, this can not necessarily be so because carbon dioxide instead of proton was eliminated in White's reaction. We present in this paper a direct experimental evidence for the *cis* elimination in the above dehydrobromination using the 2-exo-deuterio analog (**3d**) of **3**.

3-Bromo-4-homoisotwistane-2-*exo*-*d* (**3d**) was prepared by treatment of 3-hydroxy-4-homoisotwistane-2-*exo*-*d* (**2d**) with thionyl bromide. **2d**, in turn, was obtained as a minor product of the hydroboration of **1**[2a] with sodium borodeuteride. Isotopic purity of **2d** thus obtained was 89%. The exo configuration of the 2-deuterium atom in these compounds is obvious from the established exo *cis*



1 **2d** **3d** **1d**

attack of diborane on bi- and polycyclic olefins.[4] Reaction of **3d** with sodium amide in refluxing toluene gave **1**. ^{13}C NMR and IR spectroscopy could not detect deuterium in this sample of **1**. Mass spectrometry indicated the presence of only 3% 1-d_1,[5] clearly demonstrating a predominant *cis* elimination mechanism for the reaction.

References

1) J. R. Wiseman, H. Chan, and C. J. Ahola, J. Amer. Chem. Soc., **91**, 2812 (1969); J. R. Wiseman and W. A. Pletcher, J. Amer. Chem. Soc., **92**, 956 (1970).

2) (a) N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, and K. Aigami, J. Chem. Soc., Chem. Commun., 372 (1975); (b) N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, K. Aigami, and E. Ōsawa, ibid., 371 (1975).

3) M. Kim and J. D. White, J. Amer. Chem. Soc., **97**, 451 (1975).

4) G. Zweifel and H. C. Brown, Org. Reactions, **13**, 1 (1963); J. A. Marshall and H. Faubl, J. Amer. Chem. Soc., **92**, 948 (1970); R. M. Coates and J. P. Chen, Chem. Commun., 1481 (1970); H. C. Brown, I. Rothberg, and D. L. V. Jagt, J. Org. Chem., **37**, 4098 (1972); P. Wilder, Jr., A. R. Portis, Jr., G. W. Wright, and J. M. Shepherd, ibid., **39**, 1636 (1974); N. Takaishi, Y. Fujikura, and Y. Inamoto, ibid., in press.

5) Possibility of the secondary conversion of once formed **1d** into **1** was definitely excluded on the basis of no loss in deuterium from separately prepared **1d** on prolonged reaction with sodium amide in refluxing toluene.

(Received September 22, 1975)