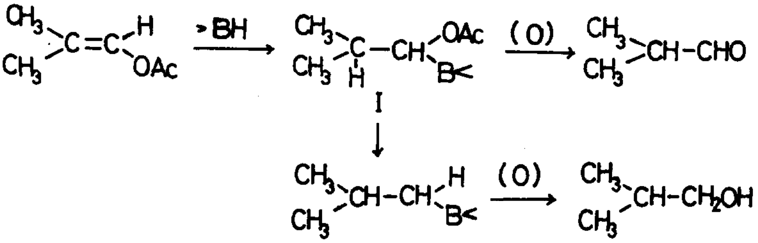
Tetrahedron Letters No.47, pp. 4937-4940, 1968. Pergamon Press. Printed in Great Britain.

HYDROBORATION OF ENOL ACETATES DERIVED FROM ALDEHYDES. NUCLEOPHILIC REDUCTION OF α-ACETOXYORGANOBORANES WITH HYDROBORATING AGENT (1)

Akira Suzuki, Kenichi Ohmori, Hidenori Takenaka and Mitsuomi Itoh
Department of Chemical Process Engineering,
Hokkaido University, Sapporo, Japan

(Received in Japan 17 July 1968; received in UK for publication 20 August 1968)

Recently it was reported that hydroboration of isobutenyl acetate with diborane places practically all of the borane in the α-position, and that the α-substituted derivative appears to be relatively stable and are readily oxidized to the corresponding aldehyde (2) as shown in equation 1. In this connection, we wish to report here that the reactions of excess diborane with enol acetates derived from aldehydes give different products, depending upon the reaction conditions, and the corresponding alcohols are obtained as the main product at relatively high reaction temperatures and for long reaction times. The results obtained in the case of isobutenyl acetate are summarized in Table 1.



1

The hydroboration was carried out by the following procedure. In a flask fitted with a thermometer, a condenser and an injection port capped with a rubber stopple under nitrogen atmosphere, was placed 30 mmoles of isobutenyl acetate. This was stirred at a definite temperature. To this solution was added 37 ml. of 6.5 N (in hydride) of diborane in tetrahydrofuran (240 mequivalent hydride). The reaction mixture was maintained at a definite temperature. At appropriate intervals of time, aliquots were removed and oxidized by the usual procedure (3). The organic layer thus obtained was then analyzed using a 20 m. Golay capillary column of Carbowax 20 M.

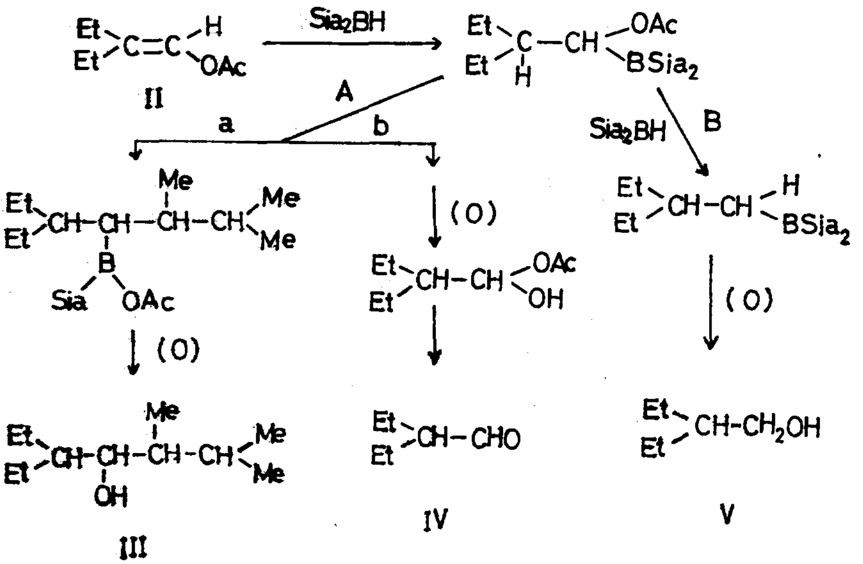
From the results, it is evident that an intermediate, α-acetoxyorganoborane (I) achieves removal of the acetoxy group and its replacement by hydrogen as indicated in equation 1, when the intermediate is reacted with excess diborane over a long reaction time or at relatively high reaction temperature.

Pasto and his co-workers previously reported such a reaction in the cases of α-alkthioxy-(4), α-alkoxy-(5) and α-haloorganoboranes (6,9). They interpreted this as "α-transfer reaction", a reaction involving an intramolecular exchange of hydrogen and other functional groups. Unfortunately, sufficient evidence has not been advanced to support the view that an intramolecular rearrangement was involved.

TABLE 1

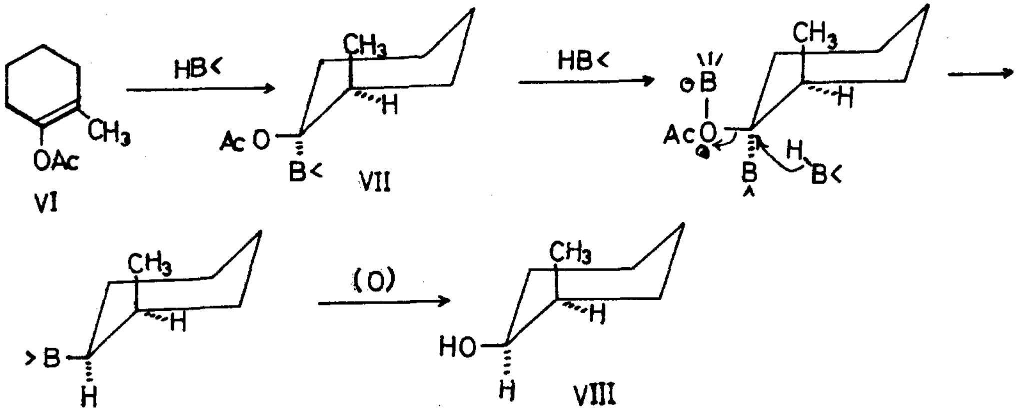
Reac.time hr.	Reac.temp. °C	Product distribution, % Isobutyl aldehyde	Product distribution, % Isobutyl alcohol	Material balance %
1	0	95	5	100
2	0	95	5	98
4	0	95	5	99
8	0	91	9	98
1	20	87	13	100
2	20	77	23	99
4	20	55	45	97
8	20	26	74	94
1	40	28	72	95
2	40	8	92	96
4	40	3	97	92
8	40	1	99	91

It was concluded here that this reaction proceeds by means of a nucleophilic reduction, based on the following reasons. As depicted in equation 2, the enol acetate (II) of diethyl acetaldehyde was hydroborated by using the excess disiamylborane in tetrahydrofuran at 20° and for 24 hrs (7). One can expect to obtain an alcohol (III) and/or diethyl acetaldehyde (IV) after oxidation, if the reaction proceeds by " α-transfer" mechanism through path A-a (rearrangement of siamyl group and hydrogen) and/or path A-b (non-rearrangement). On the other hand, if the reaction proceeds by nucleophilic reduction with another disiamylborane, 2-ethyl-1-butanol (V) should be obtained. The gas chromatographic analysis of the reaction mixture showed that the yields of V and diethyl acetaldehyde (IV) were 27 % and 39 %, respectively, and we could not find any traces of III.



2

Next, an attempt was made to hydroborate 1-methyl-2-acetoxycyclohexene (VI) by diborane in tetrahydrofuran, and then it was found that the product is essentially pure cis-2-methylcyclohexanol (VIII). This indicates that the reduction of α-acetoxyorganoborane (VII) proceeds with complete inversion. In regard to this, Pasto (6,9) proposed that the reaction with overall inversion of stereochemistry proceeds through a transfer involving an "open book" transition state, whereas the reaction with retention of stereochemistry involves a "closed book" transition. However, these mechanisms seem to require extraordinary transition, if the reaction is indeed intramolecular. On the other hand, complete inversion is readily understandable if we are dealing with a nucleophilic displacement as revealed in equation 3.



3

Further, it was observed that in the hydroboration of the enol acetate from dimethyl acetaldehyde, the amount of isobutanol in the products increases with the increase of the concentration of hydride used, as indicated in Table 2. This evidence also supports the view of a nucleophilic reduction mechanism.

TABLE 2*

H^- Concentration, N	Yield %	Product distribution, % isobutyraldehyde	isobutanol
1	100	100	trace
3	100	63	37
5	87	48	52
6.5	97	47	53

* Added H^-, H^-/olefin = 8; reac. temp. 20°; reac. time, 4 hr. The enol acetate was added to the THF solution of borane.

Wallace (8) found that diborane in tetrahydrofuran exhibits appreciable conductivity. This evidence may also support the removal of the acetoxy group by nucleophilic displacement.

REFERENCES

1. The authors gratefully acknowledge the assistance of the Phillips Petroleum Company, Bartlesville, Oklahoma for the supply of pure 2-methyl-2-butene.
2. H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, in the press.
3. G. Zweifel and H. C. Brown, "*Organic Reaction,*" **13**, 1 (1963).
4. D. J. Pasto and J. L. Miesel, *J. Am. Chem. Soc.*, **85**, 2118 (1963).
5. D. J. Pasto and C. C. Cumbo, *ibid*., **86**, 4343 (1964).
6. D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966).
7. This reaction was extraordinarily slow, as compared with the case of diborane.
8. W. J. Wallace, Ph. D. Thesis, Purdue University (1962).
9. D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, **89**, 5608 (1967).