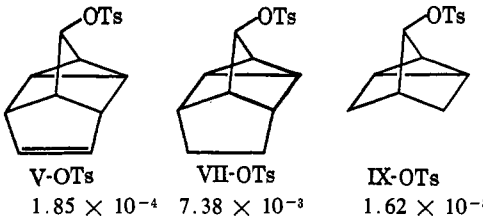
8-en-5-ol (V), bp 56–57° (0.5 mm), gives the following: nmr (δ) 1.35 (d, 2 H), 1.6–1.8 (m, 1 H), 1.85 (bs, 1 H), 2.65 (bs, 1 H), 3.10 (bs, 1 H), 3.90 (s, OH), 4.00 (t, 1 H), 5.85–6.25 (m, 2 H). The spectrum of the deuterated compound V(D) lacks only the signal at δ 4.00. Spectra of V-OH and VI were identical with those of samples prepared by two other independent routes by Coates and Kirkpatrick.[6]

To our great surprise, solvolysis of V(D)-OTs in buffered (10% molar excess of NaOAc) acetic acid at 110° for 3 hr (over 10 half-lives) led to V(D)-OAc as the sole product, *with the deuterium completely* ($\pm 2\%$) *unscrambled!* Unfortunately, attempts to study the rearrangement under more vigorous conditions (unbuffered HOAc or HCOOH) were frustrated by solvent addition to the reactive, norbornene-type double bond.[7] Acetolysis of VII-OTs also gave only unrearranged product, VII-OAc.

The double bond in V-OTs also produces a marked rate-depressing effect, as is revealed in the comparison in Chart II.

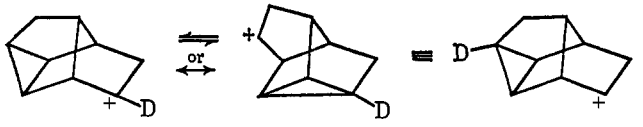
Chart II



	V-OTs	VII-OTs	IX-OTs
k, sec^{-1} (75°)	1.85×10^{-4}	7.38×10^{-3}	1.62×10^{-3}
k_{rel}	0.11	4.6	1.0
ν_{CO}, cm^{-1}	1755		1762

Although the major product from solvolysis of either 3-nortricyclyl tosylate (IX) or 5-norborn-2-enyl tosylate is 3-nortricyclyl acetate, some 5-norborn-2-enyl acetate also is formed.[7a,8] By analogy, it might have been expected that *some* conversion of I to II and eventually to III might have occurred, with attendant deuterium scrambling.[5] The nonobservance of such scrambling, at least under the conditions employed, shows that "leakage" to II (and to III) did not occur. Not only the unsaturated tosylate V-OTs, but also the saturated analog VII-OTs, failed to produce any detectable homoallylic-type product (*e.g.*, derived from II) on acetolysis. The extra two-carbon bridges in these systems render such opened products unfavorable, possibly because the additional strain introduced by these bridges is greater in the norbornene than in the nortricyclene system.

(5) *Cf.* the facile rearrangement observed by P. K. Freeman and D. M. Balls, *Tetrehedron Letters*, 437 (1967).



(6) R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **90**, 4162 (1968). This paper deals with the behavior of a related $C_9H_9^+$ system, the 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl cation. Our own work with this system (*cf.* VIII), entry to which can be gained by irradiation of V-O-*t*-Bu, will be reported in the future. We are grateful to Professor Coates for exchanges of information and for spectral comparisons.

(7) (a) S. J. Cristol, M. K. Seifert, D. W. Johnson, and J. B. Juvale, *J. Am. Chem. Soc.*, **84**, 3918 (1962); (b) S. J. Cristol and G. C. Fusco, *J. Org. Chem.*, **33**, 106 (1968).

(8) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 77, 3034 (1955).

The double bond in V-OTs produces a 40-fold rate decrease relative to VII-OTs. This decrease seems larger than would be expected on the basis of the inductive effect of such a remote group.[9] A steric effect may be responsible, at least in part. The etheno bridge in I decreases the C-1–C-7 distance. This should depress the solvolysis rate of V-OTs relative to that of IX-OTs.[11]

There is no evidence from either the rate data or the products formed of any participation of the double bond electrons in the ionization of V-OTs. Nevertheless, there is considerable anchimeric assistance in the ionization of V-OTs. From the carbonyl frequency of VI (ν_{CO} band center $\sim$1755 cm^{-1}), an acceleration of 10^5 can be estimated.[10] It would appear that there is considerable stabilization of I due to cyclopropylcarbinyl-type resonance, but without substantial opportunities for structural rearrangements to ions such as II, which might have led to deuterium label scrambling.

Under similar conditions some potentially degenerate carbonium ions rearrange extensively,[1,3,5] while others do not. We are seeking the causes for this disparate behavior, which adds to the variety we are encountering in our continuing studies of $(CH)_n^+$ systems.

Acknowledgments. This research was supported by grants from the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.

(9) The acetolysis rate of norborn-5-en-2-*endo*-yl tosylate is also 40 times slower than that of 2-*endo*-norbornyl tosylate,[10] but the double bond is closer.

(10) P. von R. Schleyer, *J. Am. Chem. Soc.*, 86, 1854, 1856 (1964); C. S. Foote, *ibid.*, 86, 1853 (1964).

(11) See P. von R. Schleyer and G. W. Van Dine, *ibid.*, 88, 2321 (1966).

(12) National Institutes of Health Predoctoral Fellow, 1965–1968.

Paul von Ragué Schleyer, Ronald E. Leone[12]
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received June 14, 1968

Reaction of Organoboranes with 2-Bromoacrolein. A Facile One-Stage Synthesis of α-Bromo Aldehydes

Sir:

Difficulties inherent in the preparation of the highly reactive α-bromo aldehydes by direct bromination of the corresponding aldehydes have led to the development of indirect synthetic methods, such as the addition of bromine to enol acetates[1] or enamines,[2] followed by hydrolysis of the intermediates. We wish to report that α-bromo aldehydes are now readily accessible by the reaction of organoboranes with 2-bromoacrolein (**1**).

$$R_3B + CH_2{=}\underset{\underset{Br}{|}}{C}CHO \xrightarrow{H_2O} RCH_2\underset{\underset{Br}{|}}{C}HCHO \qquad (1)$$

The products can be isolated from the reaction mixture by distillation at low pressures. However, they are exceedingly reactive and cannot be stored as such for any length of time. In contradiction to reports

(1) F. Bedoukian, *J. Am. Chem. Soc.*, **66**, 1325 (1944).
(2) R. Tiollais, *et al.*, *Bull. Soc. Chim. France*, 1205 (1964).

Table I. Conversion of Olefins into Substituted Aldehydes by the Reaction of the Corresponding Organoboranes with 2-Substituted Acroleins

Olefin	Product	Bp, °C (mm)	Yield, % Glpc	Yield, % Pmr	Yield, % isolated	Derivative,[c] mp, bp °C (mm)
1-Butene[a]	2-Bromoheptanal	90 (16)		100	85	DEA,[d] 74 (0.6)
2-Butene[a]	2-Bromo-4-methylhexanal	60 (4.8)		90	81	DEA,[d] 66 (0.8)
Isobutylene[a]	2-Bromo-5-methylhexanal	56 (4.0)		100	80	DEA,[d] 64 (0.5)
Cyclohexene[a]	2-Bromo-3-cyclohexylpropanal	69 (0.8)		90	65	DEA,[d] 98 (0.8)
2-Butene[b]	2,4-Dimethylhexanal	84 (25)	100		95	DNP,[e] 96.5–97.0
Isobutylene[b]	2,5-Dimethylhexanal	66 (16)	100	100	95	DNP,[e] 101.5–102
Cyclohexene[b]	2-Methyl-3-cyclohexylpropanal	99 (17)	100		92	DNP,[e] 144–145
Norbornene[b]	2-Methyl-3-norbornylpropanal	110 (17)	100		97	DNP,[e] 144.5–145

[a] Reaction of R_3B with 2-bromoacrolein. [b] Reaction of R_3B with 2-methylacrolein. [c] Satisfactory analyses for all derivatives. [d] DEA = diethyl acetal. [e] DNP = 2,4-dinitrophenylhydrazone.

in the literature,[3] it proved to be impossible to prepare the 2,4-dinitrophenylhydrazones by the usual procedures. However, conversion to the corresponding diethyl acetals was convenient, and the products could be readily analyzed and stored as such.

In representative experiments involving the reaction of organoboranes with 2-bromoacrolein, analysis of the reaction mixture by pmr, before the addition of water, revealed the complete absence of either bromoacrolein or α-bromo aldehyde. However, immediately following the addition of water, the pmr spectrum revealed an essentially quantitative yield of α-bromo aldehyde. This confirms the earlier conclusion that the reaction must involve a 1,4 addition of the organoborane to the conjugated system to produce an enol borinate which is hydrolyzed by the water to the free aldehyde.[4,5]

The following procedure is representative for the synthesis of α-bromo aldehydes. A 100-ml flask fitted with an inlet carrying a rubber septum cap, a magnetic stirring bar, and a condenser was flushed with nitrogen. In the flask was placed 50 mmol of borane in 25 ml of tetrahydrofuran solution at room temperature. Then 150 mmol of cyclohexene in 20 ml of tetrahydrofuran was added, and the mixture was stirred at 50° for 3 hr to complete formation of the tricyclohexylborane.[6] Then 4.1 ml (50 mmol) of 2-bromoacrolein[7] was added. The reaction was exothermic and the temperature rose spontaneously to 40°. After cooling to room temperature, 0.95 ml (50 mmol) of water was added and stirred for 15 min. Benzene was added as an internal standard. Pmr examination indicated a yield of 90%. Distillation gave 7.2 g (65%) of 2-bromo-3-cyclohexylpropanal, bp 68–69° (0.8 mm). The product, 5.5 g (25 mmol), was dissolved in 25 ml of tetrahydrofuran, 4.6 ml (30 mmol) of triethyl orthoformate was added, followed by one drop of methanesulfonic acid.[8] The solution was refluxed for 0.5 hr. Distillation yielded 6.0 g (85%) of the diethyl acetal of 2-bromo-3-cyclohexylpropanal, bp 98° (0.8 mm).[9]

The results are summarized in Table I.

We also examined the feasibility of utilizing 2-methylacrolein (2). Again the reaction proceeded smoothly,

$$R_3B + CH_2{=}\underset{\displaystyle CH_3}{\overset{|}{C}}CHO \xrightarrow{H_2O} RCH_2\underset{\displaystyle CH_3}{\overset{|}{C}}HCHO \qquad (2)$$

in excellent yield (Table I). The observation that both an electron-withdrawing group, such as bromine, and an electron-supplying group, such as methyl, can be accommodated in the 2 position of acrolein suggests that this synthetic route is a promising one of considerable generality.[10] It suffers from the disadvantage that only one of three alkyl groups on boron is utilized. However, we are achieving considerable success in overcoming this deficiency in the one-carbon homologation reaction[11] and in the two-carbon homologation reaction,[12] and we hope to find a solution to this problem for the present three-carbon homologation (propanalation) reaction.

(3) For example, Bedoukian[1] reported that the 2,4-dinitrophenylhydrazone of 2-bromoheptanal had mp 106° and that the analysis for nitrogen was in agreement with the proposed formula. (No analyses for other elements were reported.) We also obtained a material with mp 105.5–106°. However, the analysis revealed the absence of bromine. Compare C. Stevens and B. Gillis, *J. Am. Chem. Soc.*, 79, 3448 (1957).

(4) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, 89, 5708 (1967).

(5) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, 89, 5709 (1967).

(6) It should be pointed out that most other hydroborations go readily to completion at 25°, or even 0°.

(7) A. Berlande, *Bull. Soc. Chim. France*, 37 [4], 1385 (1925).

(8) In an alternative procedure, the triethyl orthoformate was added directly to the reaction mixture and the acetal was formed *in situ*. The residual organoboranes were then oxidized by hydrogen peroxide in the presence of excess sodium acetate and the product was distilled. This procedure results in somewhat higher recovery of the α-bromo diethyl acetal.

(9) For the α-methyl aldehydes, the procedure previously described[5] was followed except that the excess of 2-methylacrolein was reduced to 50%. Actually, the need for an excess has not yet been established. In the reactions involving 2-bromoacrolein, the theoretical quantity proved adequate to achieve nearly quantitative yields.

(10) However, crotonaldehyde and cinnamaldehyde failed to react with tri-*n*-butylborane under these conditions.

(11) H. C. Brown, R. A. Coleman, and M. W. Rathke, *J. Am. Chem. Soc.*, 90, 499 (1968).

(12) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, 90, 818 (1968).

(13) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

(14) National Science Foundation Postdoctorate Fellow at Purdue University, 1967–1968.

Herbert C. Brown, George W. Kabalka[13]
Michael W. Rathke,[14] Milorad M. Rogić
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907
Received April 3, 1968

Reaction of Organoboranes with Mannich Bases. A Convenient Procedure for the Alkylation of Cyclic and Bicyclic Ketones *via* Hydroboration

Sir:

Mannich bases derived from cyclopentanone, cyclohexanone, and norbornanone, quaternized *in situ*, react smoothly in alkaline solution with organoboranes