financial support and to Professor H. Taube, Stanford University, for encouragement.

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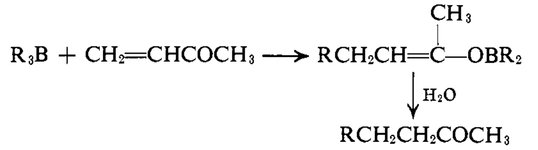
## A Facile Reaction of Organoboranes with Methyl Vinyl Ketone. A Convenient New Ketone Synthesis *via* Hydroboration

*Sir:*

We wish to report that trialkylboranes, readily available *via* hydroboration,[1] undergo a remarkably fast 1,4 addition to methyl vinyl ketone. Hydrolysis of the initially formed intermediate produces the corresponding methyl ketone I.



$$R_3B + CH_2{=}CHCOCH_3 \longrightarrow RCH_2CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}OBR_2 \xrightarrow{H_2O} RCH_2CH_2COCH_3$$

I

Indeed, both the addition and hydrolysis can be made to occur concurrently in a few minutes at 25°, providing a remarkably simple conversion of a large variety of olefins into the corresponding ketones II–VIII. Since methyl ketones are readily converted into the corresponding acids by the haloform reaction,[2] this likewise provides a simple synthesis of the corresponding carboxylic acids involving a lengthening of the chain by three carbon atoms.

$$CH_3CH_2CH{=}CH_2 \longrightarrow CH_3(CH_2)_5COCH_3$$

II

$$CH_3CH{=}CHCH_3 \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_2COCH_3$$

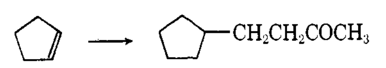
III

$$(CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_2CH(CH_2)_3COCH_3$$

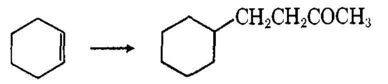
IV

$$CH_3(CH_2)_5CH{=}CH_2 \longrightarrow CH_3(CH_2)_9COCH_3$$

V



VI



VII

VIII

There is a disadvantage in that only one of the three groups on boron participates in the reaction under these mild conditions. However, this is compensated for by the remarkable speed with which the reaction occurs and the mildness of the conditions which promise to make the synthesis broadly applicable to a wide variety of structures and derivatives.

We have utilized two general procedures.

**Procedure A.** In a 200-ml flask was placed 11.2 g (100 mmoles) of 1-octene and 30 ml of tetrahydrofuran. The flask was flushed with nitrogen and 3.3 ml of a 1.00 *M* solution of borane in tetrahydrofuran was injected with a hypodermic syringe to achieve hydroboration.[3] After 1 hr, 3.5 g (50 mmoles) of methyl vinyl ketone in 15 ml of tetrahydrofuran was added and the reaction mixture was maintained at 40° for 2 hr. Then 15 ml of water was added and the solution was heated at 40° for 1 hr to hydrolyze the enol dialkylborinite intermediate. The solution was dried over magnesium sulfate. Glpc analysis indicated the formation of 31 moles of ketone, a yield of 93%, containing 2-decanone and 5-methyl-2-undecanone in an 86:14 ratio.[4]

**Procedure B.** Hydroboration was carried out as above, using 120 mmoles of 1-octene, to form 40 mmoles of the organoborane. Then 1.8 ml (100 mmoles) of water was added, followed by 4.4 g (60 mmoles) of methyl vinyl ketone. The reaction mixture was allowed to stir for 1 hr at 25°.[5] Glpc analysis indicated the presence of 39.5 mmoles of the dodecanones, a yield of 99%, in a molar ratio of 85:15.

The ketones were isolated by removal of the tetrahydrofuran under vacuum followed by a simple distillation of the reaction mixture. No difficulty was encountered in the separation from the much higher boiling boron-containing side products.

The experimental results are summarized in Table I.

**Table I.** Conversion of Olefins into 4-Alkyl-2-butanones by Reaction of the Corresponding Organoboranes with Methyl Vinyl Ketone

| | | Yield,[c,d] % | |
|---|---|---|---|
| Olefin | Product,[a] % | Procedure A | Procedure B |
| Ethylene | 2-Hexanone | 99 | |
| Propylene | 2-Heptanone[b] | 100 | |
| 1-Butene | 2-Octanone, 85 | | |
| | 5-Methyl-2-heptanone, 15 | | 99 (86) |
| 2-Butene | 5-Methyl-2-heptanone | | 80 (70) |
| Isobutylene | 6-Methyl-2-heptanone | | 65 (50)[e] |
| 1-Octene | 2-Dodecanone, 85 | | |
| | 5-Methyl-2-undecanone, 15 | 93 (85.5) | 99 (83) |
| Styrene | 6-Phenyl-2-butanone, 57 | | |
| | 5-Methyl-5-phenyl-2-pentanone, 43 | 93 | |
| Cyclopentene | 4-Cyclopentyl-2-butanone | | 99 (86) |
| Cyclohexene | 4-Cyclohexyl-2-butanone | 100 | 95 (80) |
| Norbornene | 4-(*exo*-Norbornyl)-2-butanone | | 99 (80) |

[a] All products were either compared with authentic samples or exhibited analytical data and spectra in accordance with the assigned structures. [b] Analysis for the two isomers was not made. [c] By glpc analysis. [d] Numbers in parentheses are isolated yields. [e] Reaction relatively slow; yield increased with additional time.

Hydroboration of a 1-alkene produces approximately 6% of the secondary alkyl derivative.[1] Hydroboration

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(1) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(2) R. C. Fuson and B. A. Bull. *Chem. Rev.*, **15**, 275 (1934).

(3) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(4) Clathration with urea provides a simple means of separating the major product from the branched-chain impurity.

(5) Actually, glpc examination indicated that the reaction was essentially complete in 10 min.

of styrene produces 18% of the secondary derivative.[1] Consequently, the formation of 14% 5-methyl-2-undecanone from 1-octene and 43% 5-methyl-5-phenyl-2-pentanone indicates that secondary groups have a large preference for participating in the migration as compared to the corresponding primary groups. The precise mechanism of this unusually facile reaction has many points of interest, and we plan to explore it in the future. However, at the moment it appears more urgent to establish the full scope of the reaction. It is evident that many $\alpha,\beta$-unsaturated ketones[6] should be capable of participating in this reaction, as well as many other vinyl derivatives.[7] Consequently, we are devoting our main efforts at the present time to a broad exploration of the full scope of this interesting reaction.

It is becoming evident that the organoboranes are exceedingly versatile reactants, with major possibilities in organic synthesis. Among the more interesting possibilities to which attention has already been called are: isomerization,[1] displacement,[1] contrathermodynamic isomerization of olefins,[1] cyclization[8a,b] protonolysis,[1] oxidation to alcohols (alkaline hydrogen peroxide),[1] oxidation to ketones (chromic acid),[8c] amination,[8d] metallation,[8e] coupling with alkaline silver nitrate,[1] homologation,[8f] and carbonylation[8g] to tertiary alcohols,[8h] ketones,[8i] methylol derivatives,[8j] acids,[8k] ring ketones,[8l] and polycyclics.[8m] The development described in the present publication opens the door to a new area with major promise.

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(6) The present reaction bears a number of points of resemblance to the "reductive alkylation of benzoquinone" described by M. F. Hawthorne and M. Reintjes, *J. Am. Chem. Soc.*, **87**, 4585 (1965).

(7) Actually, we have observed that trialkylboranes react with acrolein with extraordinary speed to form the corresponding aldehydes: H. C. Brown, M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1067).

(8) (a) H. C. Brown, K. J. Murray, H. Müller, and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1443 (1966); (b) R. Köster, *Angew. Chem. Intern. Ed. Engl.*, **3**, 174 (1964); (c) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2951 (1961); (d) M. W. Rathke, N. Inoue, K. R. Varma, and H. C. Brown, *ibid.*, **88**, 2870 (1966); (e) J. B. Honeycutt, Jr., and J. M. Riddle, *ibid.*, **82**, 3051 (1960); (f) J. J. Tufariello, P. Wojtkowski, and L. T. C. Lee, *Chem. Commun.*, 505 (1967); (g) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); (h) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2737 (1967); (i) *ibid.*, **89**, 2738 (1967); (j) *ibid.*, **89**, 2740 (1967); (k) H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967); (l) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967); (m) *ibid.*, **89**, 5478 (1967).

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## A Facile Reaction of Organoboranes with Acrolein. A Convenient New Aldehyde Synthesis *via* Hydroboration

*Sir:*

Trialkylboranes undergo a remarkably fast 1,4 addition to acrolein, even faster than the related reaction of trialkylboranes with methyl vinyl ketone.[1] The reaction produces an intermediate, presumably the enol borinate, whose hydrolysis yields the corresponding aldehyde (I).

$$\begin{array}{r} R_3B + CH_2{=}CHCHO \longrightarrow RCH_2CH{=}CHOBR_2 \\ \Big\downarrow {\scriptstyle H_2O} \\ RCH_2CH_2CHO \\ \text{I} \end{array}$$

We have found it more convenient to add water to the solution of the organoborane in tetrahydrofuran. Then introduction of the acrolein results in the concurrent 1,4 addition and simultaneous hydrolysis to produce the aldehyde. The reaction is extraordinarily fast. In some cases we have observed it to be essentially over in as little as 5 min at 25°. However, our standard procedure provides for a reaction time of approximately 1 hr at room temperature before recovering the aldehyde.

Aldehydes are notoriously unstable, difficult to isolate in the pure state. Consequently, they are customarily characterized as the semicarbazones or 2,4-dinitrophenylhydrazones.[2] Our initial attempts to separate the aldehydes from the residual dialkylborinic acids by simple distillation, in the manner used to isolate the corresponding methyl ketones,[1] led to obvious side reactions and loss of product. Fortunately, experiments revealed that the dialkylborinic acids did not interfere with glpc analysis for the aldehydes. Consequently, in this initial survey of the scope of this new reaction we relied on gas chromatography to establish the yield and to obtain pure samples adequate for characterization.

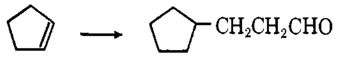
According to our initial survey, utilizing our standard list of olefins, the reaction appears to be one of wide generality, providing the aldehyde from a wide variety of structural types (II–VIII).

$$CH_3CH_2CH{=}CH_2 \longrightarrow CH_3(CH_2)_5CHO \quad \text{II}$$

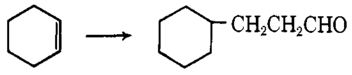
$$CH_3CH{=}CHCH_3 \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_2CHO \quad \text{III}$$

$$(CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_2CH(CH_2)_3CHO \quad \text{IV}$$

$$CH_3(CH_2)_3CH{=}CH_2 \longrightarrow CH_3(CH_2)_7CHO \quad \text{V}$$



VI



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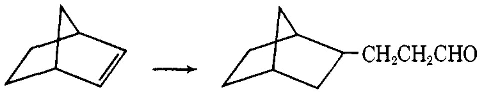

VIII

In one experiment, 20 mmoles of tri-*n*-hexylboron in anhydrous tetrahydrofuran was treated with 40 mmoles of acrolein. Analysis of the solution revealed the essential disappearance of the acrolein, but only minor amounts of nonanal. Addition of 20 mmoles

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(1) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 5708 (1967).

(2) H. C. Brown and C. P. Garg, *ibid.*, **86**, 1085 (1964); H. C. Brown and A. Tsukamoto, *ibid.*, **86**, 1089 (1964).