

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 α,β -unsaturated ketones⁶ 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.

(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 (1967).

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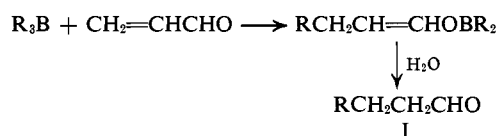
A Facile Reaction of Organoboranes with Acrolein. A Convenient New Aldehyde Synthesis via Hydroboration

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

(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).

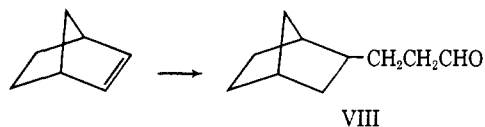
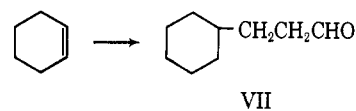
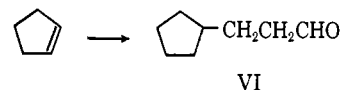
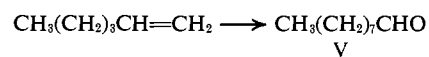
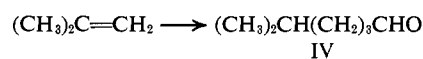
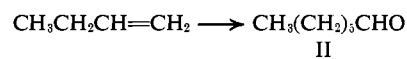
enol borinate, whose hydrolysis yields the corresponding aldehyde (I).



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).



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

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

of water led to the observation of 14 mmoles of nonanal and 2 mmoles of a minor isomer, presumably 4-methyl-octanal, arising from the minor amount of secondary alkyl groups in the borane.^{3,4} Consequently, it is quite clear that the initial reaction produces an intermediate, such as the enol borinate shown (I), which is converted to the free aldehyde only by water or some other material containing protolytic hydrogen.

The following procedure is representative. A 200-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 40 mmoles of borane in 20 ml of tetrahydrofuran solution at room temperature. Then 120 mmoles of cyclohexene in 20 ml of tetrahydrofuran was added to form the tricyclohexylborane. The mixture was stirred at 50° for 3 hr to complete the hydroboration. Then 1.8 ml (100 mmoles) of water was added, followed by 5.3 ml (80 mmoles) of acrolein.⁵ *n*-Decane was added to serve as an internal standard. The reaction mixture was allowed to stir for 1 hr at room temperature. Samples were removed at 10, 25, and 60 min and analyzed by glpc, indicating yields of 65, 71, and 77%, respectively. The identity of the product, isolated by preparative glpc chromatography, was confirmed as 3-cyclohexylpropanal by the pmr spectrum and preparation of the semicarbazone, mp 128–129°.⁶

Table I. Conversion of Olefins into 3-Alkylpropanals by Reaction of the Corresponding Organoboranes with Acrolein

Olefin	Product, %	Yield, % ^{a,b}			
		Time, min			
1-Butene	<i>n</i> -Heptanal, 85	55			
	4-Methylhexanal, 15				
2-Butene	4-Methylhexanal	75	89	96	
Isobutylene	5-Methylhexanal		85	87	
1-Hexene	<i>n</i> -Nonanal, 85	83	78	77	
	2-Methyloctanal, 15				
Cyclopentene	3-Cyclopentylpropanal	75		88	
Cyclohexene	3-Cyclohexylpropanal	65	71	77	
Norbornene	3-(<i>exo</i> -Norbornyl)propanal	67		80	

^a By glpc analysis. ^b The yield is based on the reaction producing I, with each mole of trialkylborane yielding 1 mole of aldehyde.

The experimental results are summarized in Table I.

As in the corresponding methyl vinyl ketone case, the acrolein appears to react preferentially with the secondary alkyl groups in the organoborane. Thus tributylborane from the hydroboration of 1-butene contains 6% of 2-butyl groups. Yet the reaction product contains 15% of 2-methylhexanal and 85% of heptanal. Thus most of the secondary alkyl groups present in the tributylborane have reacted. This selective reaction could be very helpful in destroying selectively the small amount of secondary alkyl derivatives produced in the hydroboration of terminal olefins, and we are exploring

(3) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

(4) Although this minor component from the 1-hexene system has not yet been fully characterized, it was established that the minor component from 1-butene, also 15%, is identical with the product from 2-butene, 4-methylhexanal. Consequently, there can be little doubt that the minor component from the tri-*n*-hexylborane arises from the 6% of 2-hexyl groups present in the hydroboration product.

(5) It was convenient to use 100% excess of the reagent, although we have no evidence that the excess is necessary.

(6) A. Skita, *Ber.*, **48**, 1693 (1915), reports for 3-cyclohexylpropanal semicarbazone mp 128°.

this possibility. It also suggests a means of achieving a far higher conversion of a given olefin to aldehyde product than the 33% now realized. This is being investigated.

In any case, the present procedure is so remarkably simple and evidently so general that it obviously has immediate utility in providing a major new route to aldehydes. Perhaps even more important at this time is the definite implication that this reaction of organoboranes with α,β -unsaturated derivatives is of very wide generality. We are currently exploring this possibility.⁷

(7) Research in progress with M. M. Rogić, M. W. Rathke, and G. W. Kabalka.

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

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

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Nonempirical Molecular Orbital Calculations on an α -Sulfinyl Carbanion

Sir:

Definite evidence has been obtained in at least one case that the electron pair in an α -sulfonyl carbanion is directed along the internal bisector of the OSO angle.¹ An exactly analogous conclusion was reached concerning an α -sulfinyl carbanion.² However, the generality of the former result has been questioned,³ and the rigor of the nmr assignments used in the latter work may be in doubt.^{4–6}

In an effort to gain further insight into the structure of an α -sulfinyl carbanion we have now made a detailed theoretical study of the hypothetical compound hydrogen methyl sulfoxide (I) and its derived carbanion (II).⁷ The calculations were performed by the LCAO–MO–SCF method using Gaussian type functions (GTF) in the basis set.⁸ A minimal basis set of 33 GTF was used for I and 32 GTF for II. These involved a single s-GTF on hydrogen, three s-, and one set of p-GTF on carbon and oxygen, and five s-, two sets of p-, and one set of d-GTF on sulfur.⁹

Figure 1 shows the total energy of I as a function of rotation about the C–S bond. It may be noted that minima and maxima appear at the skewed positions corresponding to a 21° rotation from the staggered

(1) E. J. Corey and T. H. Lowry, *Tetrahedron Letters*, **13**, 793, 803 (1965).

(2) S. Wolfe and A. Rauk, *Chem. Commun.*, 778 (1966).

(3) D. J. Cram, R. D. Trepka, and P. St. Janiak, *J. Am. Chem. Soc.*, **88**, 2749 (1966).

(4) K. W. Buck, A. B. Foster, W. D. Pardue, M. H. Quadir, and J. M. Webber, *Chem. Commun.*, 759 (1966).

(5) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).

(6) P. B. Sollman, R. Nagarajan, and R. M. Dodson, *Chem. Commun.*, 550 (1967).

(7) The theoretical description of the α -sulfonyl system is due to H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

(8) For a description of the procedure and leading references see R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, **46**, 4585 (1967).

(9) An IBM 7094-II computer was used for the calculations, each individual conformation requiring about 30 min of computer time. Similar calculations on methylsulfinyl carbanion (to be reported in our full paper) required about 60 min of computer time per conformation. Sufficient work was done on the latter system to show that the form of its potential energy surface is similar to that of II.