fluorescence quenching, are 102 and 83 M^{-1}, respectively, for I and 86 and 57 M^{-1}, respectively, for 3,10-dimethylisoalloxazine at pH 7.85 (phosphate buffer containing 5 vol % DMF, $\mu = 1.95$).[13a]

Acknowledgment. This work was supported by a grant from the National Science Foundation.

[13a] NOTE ADDED IN PROOF. Professor P.-S. Song has extended his SDN, FOD, and π_{rr} calculations to I finding the 5 carbon the most electrophilic position. Since for both isoalloxazines and 3- and 5-deazaisoalloxazines the 5 position is the most electrophilic by these criteria, he concludes that the pattern of reactivity of the oxidized flavin should be independent of the atom at the 5 position (N *vs.* C) (private communication).

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Two Novel Reactions of Monomeric Formaldehyde with Trialkylboranes. A Remarkably Rapid Elimination Diverted by Oxygen to a Free-Radical Chain Addition

Sir:

Monomeric formaldehyde at 0° reacts rapidly with tri-*n*-butylborane to produce 1-butene and methyl di-*n*-butylborinate (eq 1). In the presence of air,

$$n\text{-Bu}_3\text{B} + \text{CH}_2\text{O} \longrightarrow n\text{-Bu}_2\text{BOCH}_3 + \text{CH}_3\text{CH}_2\text{CH}{=}\text{CH}_2 \tag{1}$$

however, the reaction takes another course, producing the one-carbon homologated ester (eq 2). The latter

$$n\text{-Bu}_3\text{B} + \text{CH}_2\text{O} \xrightarrow{\text{O}_2} n\text{-Bu}_2\text{BOCH}_2\text{Bu} \tag{2}$$

reaction proceeds through a free-radical chain mechanism involving the intermediates n-Bu· and n-BuCH$_2$O·. These two reactions appear common to other trialkylboranes.

Trialkylboranes undergo a facile 1,4 addition to α,β-unsaturated carbonyl systems.[1] The reaction involves free-radical intermediates.[2] No 1,2-addition product has been detected. Indeed, simple organoboranes do not add to the carbonyl group as do other organometallics.[3] When an attempt is made to force the addition at 100 to 150°, the reaction follows a different pathway, reductive dealkylation (eq 3).[4]

$$\text{R}_3\text{B} + \text{R}_2\text{CO} \xrightarrow{\Delta} \text{R}_2\text{BOCHR}_2 + \text{olefin} \tag{3}$$

Such reactions may involve thermal decomposition of the organoborane into R$_2$BH and olefin,[5] followed by reaction of the R$_2$BH with the aldehyde or ketone.

We now wish to report what appears to be the first direct addition of a simple trialkylborane to the carbonyl group. A 100-ml flask equipped with a magnetic stirring bar and septum inlet was charged with 20 ml of mineral oil and 3.0 g of paraformaldehyde (100 mmol). This flask was connected to a dry 100-ml reaction flask, equipped with a magnetic stirring bar and a septum inlet, by a connecting tube and distillation adapter. The vacuum takeoff of the distillation adapter was connected to a mercury bubbler and the system flushed with nitrogen. The reaction flask was cooled to 0° and then charged with 20 ml of tetrahydrofuran (THF) and 10 mmol of tri-*n*-butylborane. The mineral oil was heated to 120°, slowly raised to 140°, to generate monomeric formaldehyde.[6] After 90 min the borane (gc analysis) had disappeared and a new peak corresponding to methyl di-*n*-butylborinate had appeared. This compound was isolated and identified by comparison with an authentic sample. The reaction mixture was oxidized with 10 ml of 3 *N* sodium hydroxide and 10 ml of 30% hydrogen peroxide. Analysis by gc revealed 20.1 mmol of 1-butanol, 0.3 mmol of 1-pentanol, and 0.2 mmol of tetrahydrofurfuryl alcohol.

The small amount of 1-pentanol indicated that some addition of the tri-*n*-butylborane to the formaldehyde had occurred. The concurrent formation of the tetrahydrofurfuryl alcohol from the solvent suggested that the reaction might involve free-radical intermediates. Many free-radical reactions of organoboranes may be initiated by oxygen.[7] When the reaction was repeated and air added at 1–2 ml per min through a syringe needle directly above the THF solution, the reaction followed an entirely new path. Oxidation after 90 min produced 20.3 mmol of 1-butanol, 7.8 mmol of 1-pentanol, and 2.6 mmol of tetrahydrofurfuryl alcohol. The use of benzene avoided the formation of the side product.

The presence of iodine[8] (5 mol %) or copper *N,N*-diethyldithiocarbamate[9] completely inhibits the formation of the homologated alcohol without affecting the reductive dealkylation. Therefore, the homologation must proceed *via* a free-radical chain reaction while the dealkylation follows a nonradical process.

Oxygen reacts with trialkylboranes to produce alkyl radicals (eq 4). These can add to formaldehyde (eq 5),[10] producing alkoxy radicals capable of displacing alkyl radicals from the organoboranes[11] (eq 6).

$$\text{R}_3\text{B} + \text{O}_2 \longrightarrow \text{R}_2\text{BO}_2\cdot + \text{R}\cdot \tag{4}$$

$$\text{R}\cdot + \text{CH}_2\text{O} \longrightarrow \text{RCH}_2\text{O}\cdot \tag{5}$$

$$\text{RCH}_2\text{O}\cdot + \text{R}_3\text{B} \longrightarrow \text{R}_2\text{BOCH}_2\text{R} + \text{R}\cdot \tag{6}$$

The mild conditions of the reductive dealkylation suggest that it cannot involve prior dissociation of the organoborane. Instead, the reaction presumably proceeds through a six-member ring transition state similar to that proposed for the rapid dealkylation of organoboranes with *cis*-azobenzene[12] (eq 7). The precise reason why the reaction course is so different for formaldehyde and higher aldehydes is not yet clear.

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[1] H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **93**, 3777 (1971), and references cited therein.

[2] G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *ibid.*, **92**, 710 (1970).

[3] Certain organoboranes containing allylic or benzylic alkyl groups do undergo a facile addition to carbonyls: B. M. Mikhailov and Y. N. Bubnov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1874 (1964).

[4] B. M. Mikhailov, Y. M. Bubnov, and V. G. Kiselev, *Zh. Obshch. Khim.*, **36**, 62 (1966).

[5] L. Rosenblum, *J. Amer. Chem. Soc.*, **77**, 5016 (1955).

[6] J. F. Walker, "Formaldehyde," Reinhold, New York, N. Y., 1953.

[7] A. Suzuki, N. Miyaura, M. Itoh, H. C. Brown, G. W. Holland, and E. Negishi, *J. Amer. Chem. Soc.*, **93**, 2792 (1971), and references cited therein.

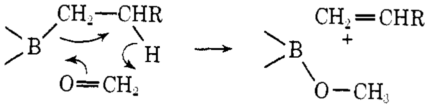
[8] M. M. Midland and H. C. Brown, *ibid.*, **93**, 1506 (1971).

[9] A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 17 (1967).

[10] G. Fuller and F. F. Rust, *J. Amer. Chem. Soc.*, 80, 6148 (1958).

[11] A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. B*, 1823 (1971).

[12] A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 2*, 803 (1972).



(7)

Tri-*n*-octylborane reacts similarly, producing 85% of 1-octene in the absence of air. In the presence of air 79% of the homologated alcohol was obtained (with 10% 1-octene).

In the absence of air triisobutylborane (10 mmol) reacts within 1 hr. Oxidation produced 20 mmol of isobutyl alcohol and no homologated alcohol. Consequently, one alkyl group had been eliminated by the formaldehyde. In the presence of air, the homologated product (29%) was formed.

Tri-*sec*-butylborane reacts only slowly at 0° in the absence of air. In the presence of 5 mol % of iodine, no borane was observed to react over a 4-hr period. Presumably the borane is sufficiently hindered so as to resist formation of the cyclic transition state. At a higher temperature, 120° in diglyme, a facile dealkylation takes place to give methyl di-*n*-butylborinate. At 0°, air induces the chain reaction, providing the homologated product, 2-methyl-1-butanol (45%).

Thus primary alkylboranes react quite readily through the nonradical path, while the more hindered secondary alkylboranes react only sluggishly. The straight-chain boranes also react readily by the free-radical path, but branching in the alkyl group reduces the yield of the homologated product.

Carbonylation of 9-alkyl-9-borabicyclononane reagents provides an efficient general route for the one-carbon homologation of olefins.[13] Consequently, the formaldehyde reaction is primarily of theoretical interest. It is the first example of a direct addition of an organoborane to a carbonyl group. Moreover, it is of interest that the reaction with monomeric formaldehyde can be directed to either the free-radical or nonradical mechanism. This suggests that other reactions of organoboranes may be controlled to follow both radical and nonradical pathways. We are continuing to explore these possibilities.

(13) H. C. Brown, E. F. Knights, and R. A. Coleman, *J. Amer. Chem. Soc.*, **91**, 2144 (1969).

(14) National Science Foundation Predoctoral Fellow, 1970–1972.

(15) Graduate research assistant on Grant No. GP 27742X from the National Science Foundation.

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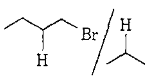
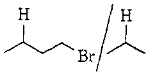
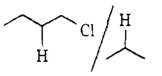
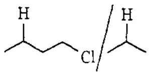
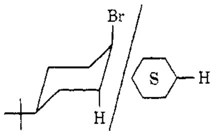
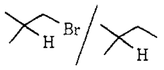
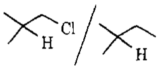
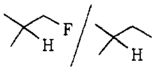
Anchimeric Assistance in Radical Brominations of Bromoalkanes. Bridged Transition State. Contradiction of Claims by Tanner, *et al.*

Sir:

To obtain further evidence for anchimeric assistance in bromine atom attack on the β hydrogens of alkyl bromides,[1] a series of competition photobrominations were examined in which the substrates were alkanes and bromoalkanes of similar structure. The reaction system consisted of substrates, *N*-bromosuccinimide (NBS) and bromine in methylene chloride solvent.[2] These solutions were degassed and then irradiated in a constant temperature bath with a tungsten filament lamp. The results of these reactions are shown in Table I.

Table I. Relative Rates of Hydrogen Abstraction by Bromine Atoms

Reactants	T, °C	$(k_X/k_H)_{obsd}$
	60	1.4
	30	2.5
	0	4.1
	−23	7.2
	60	0.35
	30	0.37
	0	0.34
	−23	0.32
	60	0.092
	30	0.25
	30	19.2 (115 per H)[a]
	35	8.0
	35	0.4[b]
	35	0.036[b]

[a] Photobromination of *cis*-4-*tert*-butylcyclohexyl bromide yields *trans*-1,2-dibromo-*cis*-4-*tert*-butylcyclohexane: P. S. Skell and P. D. Readio, *J. Amer. Chem. Soc.*, **86**, 3334 (1964). [b] Unpublished work of D. C. Lewis, this laboratory.

In all of the reactions studied, hydrogen abstraction is faster at a position β to a bromine substituent than for the corresponding alkane. The relative reactivities do not parallel those which would be predicted on the basis of simple inductive theory. Reactivity of hydrogen atoms for a straight chain alkyl bromide would be expected to increase with increasing distance between the electronegative substituent and the site of substitution, finally reaching a value characteristic for alkanes. For example, the 3 position of 1-bromobutane is 0.37 times as reactive as that of an unsubstituted secondary hydrogen of propane. One would predict that the reactivity at the 2 position of 1-bromobutane should be further reduced by a factor of at least 1/2.7 = 0.37.[3] Thus, the 2 position should be 0.37 × 0.37 = 0.14 times as reactive as propane. The observed relative rate (2.5 at 30°) is 18 times what would be expected from inductive effects.

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(1) W. A. Thaler, *J. Amer. Chem. Soc.*, **85**, 2607 (1963).

(2) The reaction between hydrogen bromide and NBS has been found to be rapid and complete under the conditions employed. These results are forthcoming in a full paper on this work.

(3) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4231 (1953).