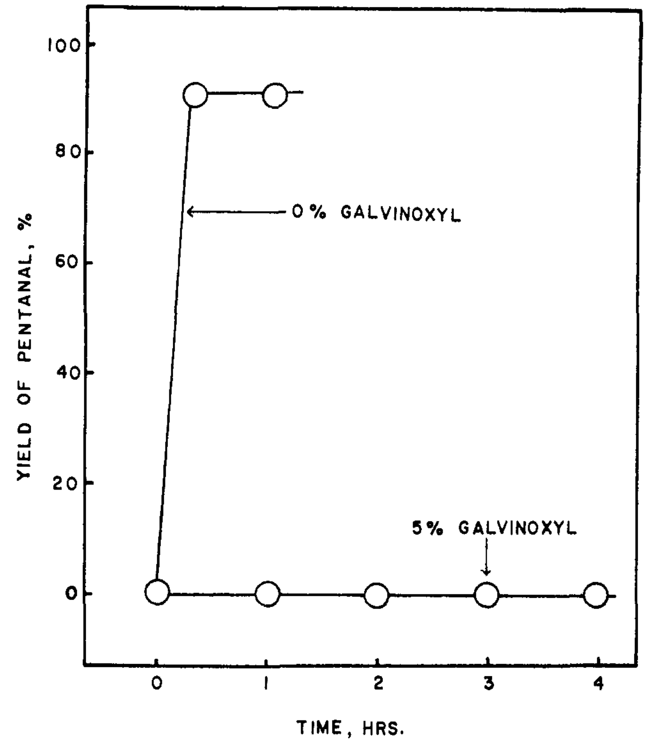


Figure 1. Reaction of acrolein (2.0 *M*) with triethylboron (1.0 *M*) in diglyme at 25°. The effect of added galvinoxyl (in mol %).

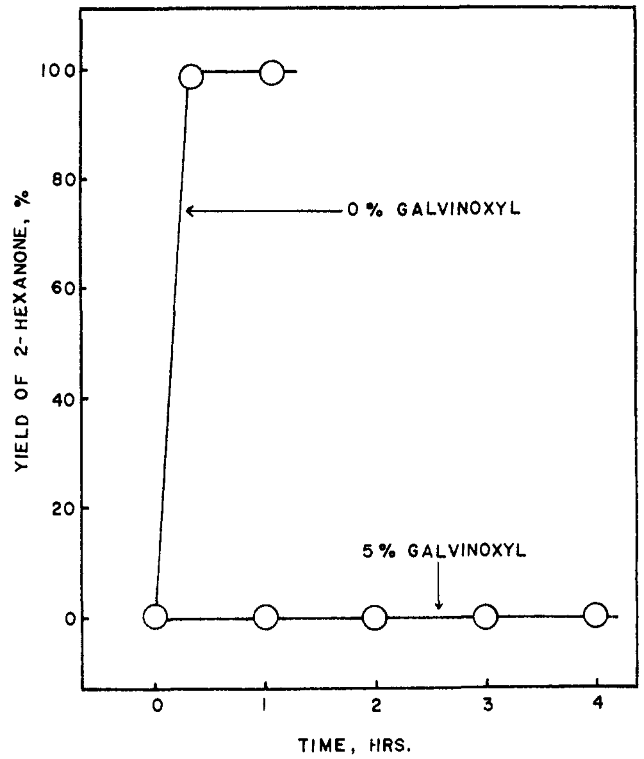


Figure 2. Reaction of methyl vinyl ketone (2.0 *M*) with triethylboron (1.0 *M*) in diglyme at 25°. The effect of added galvinoxyl (in mol %).

tion was then repeated, except that 0.5 mmol (0.21 g) of galvinoxyl was added to the organoborane just prior to the addition of the acrolein. Glpc analysis revealed that no pentanal had formed even after 12 hr, and that the reaction mixture contained 10 mmol of triethylborane and 19 mmol of acrolein.

The results of these studies are shown graphically in Figures 1 and 2.

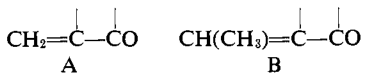
Consequently, the 1,4 addition of trialkylboranes to α,β-unsaturated carbonyl compounds must be a radical-chain reaction. The mechanism evidently proceeds through the addition of a radical to the carbon–carbon double bond of the carbonyl compound (eq 8), producing a radical intermediate 7. In the absence of a reactive organoborane this intermediate would add to the monomer through carbon to initiate a typical vinyl polymerization.[14] However, in the presence of free trialkylborane, this intermediate (7) evidently reacts through the oxygen atom to form the enol borinate with its very strong boron–oxygen bond (eq 9).[15] This enol borinate then hydrolyzes to form the desired product.

$$\mathrm{R\cdot + CH_2{=}CHCHO \longrightarrow RCH_2\dot{C}HCHO \updownarrow RCH_2CH{=}CHO\cdot} \quad (8)$$

7

$$\mathrm{7 + R_3B \longrightarrow RCH_2CH{=}CHOBR_2 + R\cdot} \quad (9)$$

Evidently the kinetic chain length for the addition of a free radical to a terminal unsubstituted grouping (A) is much longer than for the corresponding addition to the substituted grouping (B). Consequently, the reactions of organoboranes with the derivatives which contain such an unsubstituted grouping (eq 1–6) proceed spontaneously, or are catalyzed by the presence of mere traces of catalysts, whereas the substituted derivatives (**1–5**) fail to react under the same conditions. Indeed, when triethylborane was added to a reaction mixture containing both methyl vinyl ketone and *trans*-3-penten-2-one (**2**), the methylvinyl ketone reacted, but the *trans*-3-penten-2-one remained essentially unchanged. Fortunately, we have discovered means of catalyzing the reaction of such molecules which fail to undergo the apparent spontaneous reactions 1–6.[16]



$$\mathrm{CH_2{=}\overset{|}{C}{-}\overset{|}{C}O} \qquad \mathrm{CH(CH_3){=}\overset{|}{C}{-}\overset{|}{C}O}$$

A B

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[14] F. J. Welch, *J. Polymer Sci.*, **61**, 243 (1962).

[15] A. G. Davies and B. P. Roberts, *Chem. Commun.*, 699 (1969), have shown by esr that alkoxy radicals can displace an alkyl radical from a boron center, a reaction analogous to reaction 9. See also, P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3944 (1969).

[16] H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 712, 714 (1970).

[17] Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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The Acyl Peroxide and Photochemical Induced Reactions of Organoboranes with the Inert α,β-Unsaturated Carbonyl Derivatives

Sir:

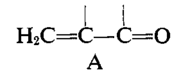
Trialkylboranes undergo a remarkably fast, spontaneous addition to many α,β-unsaturated carbonyl

Table I. Conversion of Olefins into β-Substituted Aldehydes and Ketones by the Diacetyl Peroxide and Photochemical Induced Reactions of Organoboranes with Representative β-Substituted α,β-Unsaturated Carbonyl Compounds

Organoborane from olefin	Carbonyl compound[b]	Product	Bp, °C (mm)	Yield, %: Diacetyl peroxide	Yield, %: Photo-chemical	Derivative[c,d] mp, °C
Ethylene[a]	Ethylideneacetone	4-Methyl-2-hexanone	140 (743)	88	85	DNP 43–45
Cyclohexene	Ethylideneacetone	4-Cyclohexyl-2-pentanone	64 (0.8)	90	96	DNP 110–111
Ethylene[a]	Crotonaldehyde	3-Methylpentanal	118 (747)	48	60	SC 126–127.5
Cyclohexene	Crotonaldehyde	3-Cyclohexylbutanal	62 (2.0)	86	100	DNP 127–128
Ethylene[a]	2-Cyclohexenone	3-Ethylcyclohexanone	190 (732)	56	95	SC 172–172.5
Cyclohexene	2-Cyclohexenone	3-Cyclohexylcyclohexanone	96 (0.8)	62	100	DNP 190–191

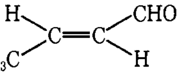
[a] Commercial triethylborane was used. [b] Excess carbonyl compound was used: 30 mmol per 10 mmol of R_3B for the diacetyl peroxide runs and 20 mmol per 10 mmol of R_3B for the photochemical experiments. [c] Satisfactory elementary analyses were obtained for all derivatives. [d] DNP = 2,4-dinitrophenylhydrazone; SC = semicarbazone.

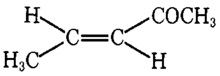
derivatives, including methyl vinyl ketone,[1] isopropenyl methyl ketone,[2] acrolein,[3] α-methylacrolein,[4] α-bromoacrolein,[4] and 2-methylenecyclanones.[5] These derivatives constitute the "reactive" group. All of these derivatives contain an unsubstituted terminal group, A.


$H_2C{=}\overset{|}{C}{-}\overset{|}{C}{=}O$

A

On the other hand, derivatives containing one or more alkyl substituents in the terminal group, such as *trans*-crotonaldehyde (**1**), *trans*-3-penten-2-one (ethylideneacetone) (**2**), mesityl oxide (**3**), 2-cyclohexen-1-one (**4**), and 1-cyclohexenyl methyl ketone (**5**), fail to react under the usual conditions.[2] These derivatives constitute the "inert" group.


1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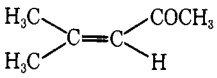
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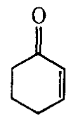
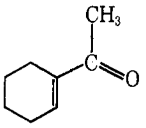

4


5

The discovery that galvinoxyl,[6] an efficient free-radical scavenger, completely inhibits the unusually facile reactions of trialkylboranes with acrolein and methyl vinyl ketone[2] suggested the possibility that these reactions must proceed through a free-radical chain mechanism. If so, the behavior of the "inert" group might be the result of a shorter chain length and inefficient initiation. Consequently, we undertook to explore the possibility of achieving a successful reaction with efficient free-radical initiators. The three representative derivatives, **1**, **2**, and **4**, were selected for this study.

We now wish to report that addition of trialkylboranes to these members of the "inert" group can be readily achieved by the addition of catalytic quantities of diacyl peroxides or by photochemical activation.

We previously reported that no significant reaction was observed between triethylborane and ethylideneacetone in diglyme solution at 25, 75, or 125° over extended periods of time, up to 24 hr.[2] However, the presence of small quantities of added benzoyl peroxide in the reaction mixture brought about a moderately rapid 1,4 addition of the triethylborane at 75° (Figure 1).

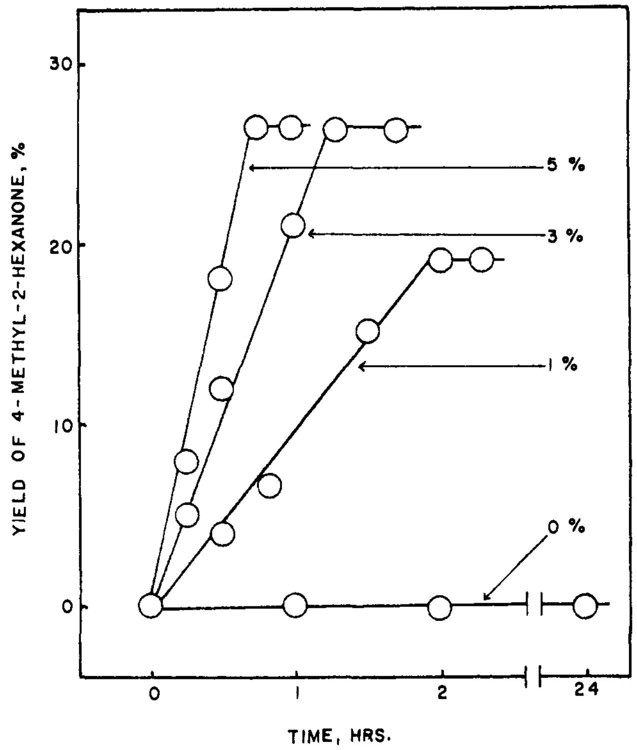


Figure 1. Reaction of triethylboron (1.0 *M*) with ethylideneacetone (1.0 *M*) at 75° in diglyme in the presence of various amounts of benzoyl peroxide (in mol %).

Unfortunately, the yields based on the organoborane were poor. The reactions apparently ceased when only 20 to 30% of the ethylideneacetone had been converted into the desired product. Investigation revealed the absence of triethylborane at this point. It was concluded that benzoic acid, formed in the decomposition of the peroxide, was catalyzing a competitive protonolysis of the organoborane.[7]

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

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

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

(4) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968).

(5) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4166 (1968).

(6) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

(7) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).

This difficulty was overcome by using a more reactive diacyl peroxide, diacetyl peroxide, at 25°. Under these conditions the catalyzed hydrolysis of the organoborane became much less important, and yields of the 1,4-addition compounds as high as 90%, based on the organoborane, were realized.

The following procedure is representative of these studies of the peroxide-catalyzed reaction. A 25-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 1.42 ml (10 mmol) of triethylborane in 10 ml of diglyme, followed by 2.94 ml (30 mmol) of ethylideneacetone and 0.18 ml (10 mmol) of water. Then 3 mol % of diacetyl peroxide (0.12 ml of a 25% solution in dimethyl phthalate[8]) was added. The solution was stirred at room temperature and samples were removed periodically and analyzed by glpc. After 24 hr, the analysis indicated that 8.8 mmol, a yield of 88%, of 4-methyl-2-hexanone was present.[9]

The experimental results are summarized in Table I.

The α,β-unsaturated carbonyl compounds used in this study absorb in a readily accessible region of the ultraviolet spectrum, namely 311 to 320 mμ.[10,11] Consequently, it appeared that such photoactivation might circumvent the carboxylic acid catalyzed hydrolysis of the organoborane and lead to improved yields. This was indeed realized.

The experimental procedure was essentially that described for the diacetyl peroxide induced reaction, except that the amount of the α,β-unsaturated carbonyl component was reduced to 20 mmol and isopropyl alcohol was utilized as the reaction medium, for reasons to be discussed later. The reaction flask containing the reaction mixture was immersed in a water bath and an external ultraviolet light source[12,13] was used. These experimental results are also included in Table I.

Our initial photochemically induced reactions were carried out in the usual aqueous tetrahydrofuran or diglyme media. However, we observed that the yields averaged 5 to 10% higher in isopropyl alcohol as the reaction medium. Consequently, this solvent was utilized for the photochemical experiments reported in Table I. Possibly the isopropyl alcohol serves to avoid or to minimize the abstraction of α-hydrogen that has been postulated to occur in the free-radical reactions of boranes.[14,15]

The peroxide or photochemically induced addition of organoboranes to the "inert" α,β-unsaturated carbonyl derivatives makes available practical new synthetic routes to a large number of compounds not previously accessible by this convenient addition reaction. The discovery that it was possible to catalyze such 1,4 additions with small amounts of oxygen[16] appeared to provide an even more convenient route. Consequently, a more detailed study of the scope of such 1,4 additions to the "inert" group was restricted to the oxygen-catalyzed reaction.[16]

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[8] Available as a 25% solution of diacetyl peroxide in dimethyl phthalate from the Lucidol Division, Wallace and Tierman, Inc., Buffalo, N. Y.

[9] The yield was 58% when the theoretical quantity of ethylideneacetone, 10 mmol, was used.

(10) J. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood, N. J., 1965, p 12.

(11) Control experiments revealed that trialkylboranes are transparent to ultraviolet light in the 280–400-mμ region.

(12) A commercially available Sears 250-W sunlamp was used in most of this phase of the investigation, and no attempt was made to filter out the extraneous visible light.

(13) The quantum yield of the reaction of crotonaldehyde with tricyclohexylborane was found to be 6 at 313 mμ (at 18% conversion). For this measurement a Bausch & Lomb Model SP-200 ultraviolet-visible grating monochronometer with 250-W Hanovia mercury arc was used as the light source (intensity measured as 3.13 × 10⁶ photons/sec). We are indebted to Dr. H. Morrison and S. R. Kurowsky for assistance with this measurement.

(14) J. C. Perrine and R. N. Keller, *J. Amer. Chem. Soc.*, 80, 1823 (1958).

(15) L. Zeldin and P. R. Girardot, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 15 N.

(16) H. C. Brown and G. W. Kabalka, *J. Amer. Chem. Soc.*, **92**, 714 (1970).

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

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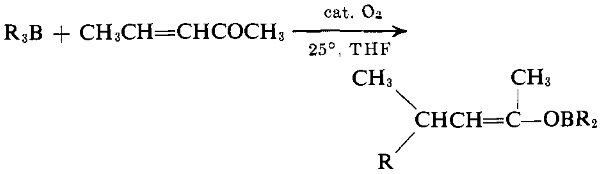
The Oxygen-Induced Reactions of Organoboranes with the Inert α,β-Unsaturated Carbonyl Derivatives. A Convenient New Aldehyde and Ketone Synthesis *via* Hydroboration

Sir:

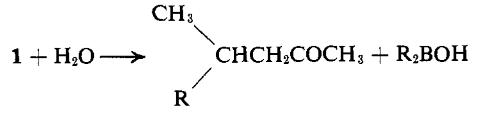
Trialkylboranes, readily available *via* hydroboration,[1] readily undergo 1,4 addition to α,β-unsaturated carbonyl compounds. The addition apparently involves a free-radical mechanism of long chain length.[2] Many α,β-unsaturated carbonyl compounds, the "reactive" group, undergo a rapid reaction with the organoborane, without added catalysts. However, other α,β-unsaturated carbonyl compounds, the "inert" group,[3] fail to react in the absence of added catalysts, such as diacyl peroxides or photochemical activation.[4]

We now wish to report that the 1,4 addition of organoboranes to this "inert" group of α,β-unsaturated carbonyl compounds is readily and conveniently achieved by introducing small quantities of oxygen (air) into the reaction mixture (eq 1). Hydrolysis of the initially formed intermediate, the enol borinate **1**, produces the desired product (eq 2).



$$R_3B + CH_3CH{=}CHCOCH_3 \xrightarrow[25°,\ THF]{cat.\ O_2} (CH_3)(R)CHCH{=}C(CH_3){-}OBR_2 \quad (1)$$

1



$$\mathbf{1} + H_2O \longrightarrow (CH_3)(R)CHCH_2COCH_3 + R_2BOH \quad (2)$$

It has been demonstrated that the autoxidation of organoboranes proceeds through a free-radical mechanism.[5,6] Consequently, it appeared to us that the addi-

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

(2) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Amer. Chem. Soc.*, **92**, 710 (1970).

(3) This "inert" group appears to be characterized by having an alkyl substituent on the terminal position of the double bond.

(4) H. C. Brown and G. W. Kabalka, *J. Amer. Chem. Soc.*, **92**, 712 (1970).

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

(6) P. G. Allies and P. B. Brindley, *Chem. Ind.* (London), 19 (1968).