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 × 10^6 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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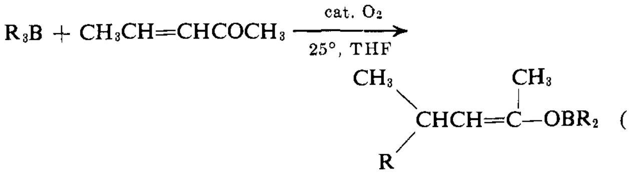
The Oxygen-Induced Reactions of Organoboranes with the Inert α,β-Unsaturated Carbonyl Derivatives. A Convenient New Aldehyde and Ketone Synthesis *via* Hydroboration

Sir:

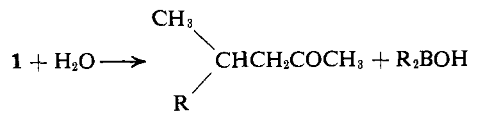
Trialkylboranes, readily available *via* hydroboration,[1] readily undergo 1,4 addition to α,β-unsaturated carbonyl compounds. The addition apparently involves a free-radical mechanism of long chain length.[2] Many α,β-unsaturated carbonyl compounds, the "reactive" group, undergo a rapid reaction with 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).



$$R_3B + CH_3CH{=}CHCOCH_3 \xrightarrow[25^\circ,\ \mathrm{THF}]{\mathrm{cat.\ O_2}} \underset{R}{\overset{CH_3}{>}}CHCH{=}\overset{\overset{CH_3}{|}}{C}{-}OBR_2 \qquad (1)$$

1



$$\mathbf{1} + H_2O \longrightarrow \underset{R}{\overset{CH_3}{>}}CHCH_2COCH_3 + R_2BOH \qquad (2)$$

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).

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

Organoborane from olefin	Carbonyl compound	Product	Bp, °C (mm)	Yield, %	Derivative[c,d] mp, °C
Ethylene[a,b]	Ethylideneacetone	4-Methyl-2-hexanone	140 (743)	70	DNP 43–44
1-Butene[b]	Ethylideneacetone	4-Methyl-2-octanone, 90% 4,5-Dimethyl-2-heptanone, 10%	90 (40)	72	SC 76–78
Cyclohexene	Ethylideneacetone	4-Cyclohexyl-2-pentanone	64 (0.8)	96	DNP 110–111
Cyclopentene	Ethylideneacetone	4-Cyclopentyl-2-pentanone	55 (1)	98	SC 126–128
Ethylene[a,b]	Crotonaldehyde	3-Methylpentanal	118 (747)	50	SC 126–127.5
1-Butene[b]	Crotonaldehyde	3-Methylheptanal, 90% 3,4-Dimethylhexanal, 10%	78 (28)	60	DNP 61.5–63
2-Butene	Crotonaldehyde	3,4-Dimethylhexanal	87 (30)	90	DNP 77–78.5
Isobutylene[b]	Crotonaldehyde	3,5-Dimethylhexanal		50	DNP 83.5–84.5
Cyclohexene	Crotonaldehyde	3-Cyclohexylbutanal	62 (2)	96	DNP 127–128
Ethylene[a,b]	2-Cyclohexenone	3-Ethylcyclohexanone	190 (732)	50	SC 172–172.5
Cyclopentene	2-Cyclohexenone	3-Cyclopentylcyclohexanone	82 (1)	96	DNP 171–172
Cyclohexene	2-Cyclohexenone	3-Cyclohexylcyclohexanone	96 (0.8)	86	DNP 190–191
Ethylene	2-Cyclopentenone	3-Ethylcyclopentanone	158 (747)	68	DNP 76.5–77.5
Cyclopentene	2-Cyclopentenone	3-Cyclopentylcyclopentanone	110 (8)	85	SC 198.5–199

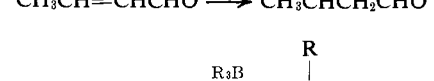
[a] Commercial triethylborane was used. [b] A 50% excess of the organoborane was used. [c] Satisfactory elementary analyses were obtained for all derivatives. [d] DNP = 2,4-dinitrophenylhydrazone; SC = semicarbazone.

tion of controlled amounts of oxygen to a reaction mixture of the organoborane and the "inert" carbonyl component might serve to initiate the desired 1,4 addition in place of the added peroxide or photochemical activation previously utilized to induce the reaction. Indeed, when a slow stream of air was passed over a solution of triethylborane and ethylideneacetone in aqueous tetrahydrofuran, a 70% yield of 4-methyl-2-hexanone was realized.

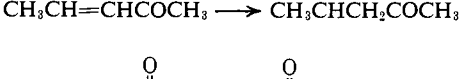
It is essential to add the air slowly, in controlled amounts. In experiments in which oxygen was added rapidly, oxidation of the organoborane became the dominant reaction and only a minor amount of 1,4 addition was realized. It is, of course, known that the direct reaction of organoboranes with oxygen is exceedingly rapid.[7,8]

Even when the oxygen is added slowly, some of the organoborane is lost through oxidation. However, it is easily possible to compensate for this by adding an excess of the organoborane.

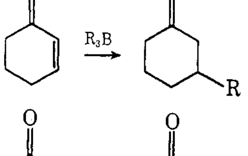
The reaction appears to be one of wide generality, accommodating a wide variety of organoboranes and "inert" α,β-unsaturated carbonyl compounds, to yield the corresponding β-substituted aldehydes and ketones in excellent yield (eq 3–6).



$$CH_3CH{=}CHCHO \xrightarrow{R_3B} CH_3\overset{R}{\overset{|}{C}}HCH_2CHO \qquad (3)$$



$$CH_3CH{=}CHCOCH_3 \xrightarrow{R_3B} CH_3\overset{R}{\overset{|}{C}}HCH_2COCH_3 \qquad (4)$$



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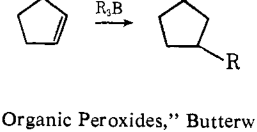

(6)

The highest yields were realized in alcohol and aqueous ether solvents. Just as in the corresponding photochemical reaction,[4] isopropyl alcohol appears to give the highest yields. These yields in aqueous tetrahydrofuran were slightly lower, but still highly satisfactory. However, in nonhydrolytic solvents, under anhydrous conditions, the yields decreased seriously. Presumably, the enol borinate **1** is itself susceptible to free-radical attack, and this side reaction is minimized by *in situ* hydrolysis of the enol borinate to the desired product.

The following procedure is representative. 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 11 mmol of borane in 10 ml of tetrahydrofuran. Then 3.3 ml (33 mmol) of cyclohexene was added to form the tricyclohexylborane. (The mixture was stirred at 50° for 3 hr to ensure completion of this exceptionally sluggish hydroboration.) Then 0.36 ml of water (20 mmol) was added, followed by 1.42 ml (10 mmol) of ethylideneacetone. Then air was passed into the flask at a rate of 1 ml/min through a syringe needle placed through the rubber septum cap to a point just above the reaction mixture. The solution was allowed to stir at room temperature. Samples were removed periodically and analyzed by glpc. Analysis after 1 hr (60 ml of air or 0.5 mmol of O_2 was introduced) indicated that 9.6 mmol (a yield of 96%) of 4-cyclohexyl-2-pentanone had been formed.

The experimental results are summarized in Table I.

It is becoming evident that organoboranes are exceedingly versatile reagents, with major possibilities in organic synthesis. Among the more interesting possibilities to which attention has already been called are: isomerization,[1] displacement,[1] cyclization,[9a,b] proton-

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(7) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961.

(8) S. Mirviss, *J. Amer. Chem. Soc.*, 83, 3051 (1961).

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olysis,[1] oxidation to alcohols,[1] oxidation to ketones,[9c] amination,[9d] metalation,[9e] coupling with alkaline silver nitrate,[1] homologation,[9f] carbonylation[9g] to tertiary alcohols,[9h] ketones,[9i] aldehydes,[9j,k] methylol derivatives,[9l] acids,[9m] ring ketones,[9n] and polycyclics,[9o] propanalation,[9p–s] alkylation of α-halo-substituted esters[9t–v] and ketones,[9w–y] and the cyclopropane synthesis.[9z]

With the exception of the coupling reaction and the catalyzed propanalation reactions here described, these reactions appear to involve largely ionic or molecular pathways. The discovery that organoboranes can be made to participate in such clean free-radical addition processes opens up a major new area for exploration. Such a study is in progress.

(j) H. C. Brown, R. A. Coleman, and M. W. Rathke, *J. Amer. Chem. Soc.*, **90**, 499 (1968); (k) H. C. Brown, E. F. Knights, and R. A. Coleman, *ibid.*, **91**, 2144 (1969); (l) M. W. Rathke and H. C. Brown, *ibid.*, **89**, 2740 (1967); (m) H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967); (n) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967); (o) H. C. Brown and E. Negishi, *ibid.*, **89**, 5478 (1967); (p) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **89**, 5708 (1967); (q) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); (r) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968); (s) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4166 (1968); (t) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818 (1968); (u) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 1911 (1968); (v) H. C. Brown and M. M. Rogić, *ibid.*, **91**, 2146 (1968); (w) H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **90**, 6218 (1968); (x) H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969); (y) H. C. Brown and M. M. Rogić, *ibid.*, **91**, 4304 (1969); (z) H. C. Brown and S. Rhodes, *ibid.*, **91**, 2149 (1969).

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

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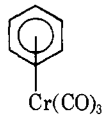
Bond Localization in Aromatic–Iron Carbonyl Complexes

Sir:

The X-ray structural analysis of benzene–chromium tricarbonyl reveals that within experimental error the C–C bond distances of the benzene ring are equal[1,2] (1.40 Å). This molecule is then satisfactorily represented as in structure I, in which, by the standard convention, the circle implies uniform electron delocalization in the ring. We wish to report that in certain aromatic complexes containing the iron tricarbonyl moiety there is, in contrast to the above, a large degree of bond fixation in the ligand. This implies significant loss of π-electron delocalization, and the ligands are then better regarded as derivatives of 1,3,5-cyclohexatriene rather than of benzene.

Our interest in the present work stemmed from attempts to assign a suitable structural formula to *p*-divinylbenzene–diiron hexacarbonyl. This compound was first described by Stone and coworkers,[3] but, at the time it was reported, insufficient data were available to allow a detailed formulation. Using the effective atomic number rule as a guideline, several structures could be contemplated for this system. With an



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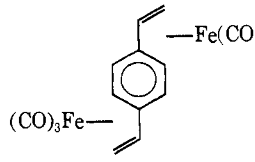

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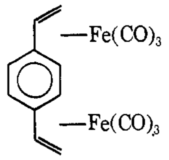

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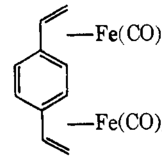
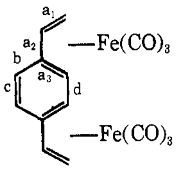


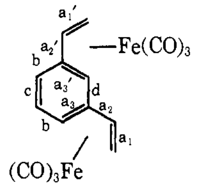
IV

"aromatic" formulation analogous to I there is structure II or III; on the other hand, if classical structures were to be used then only formula IV is possible and a disposition of atoms similar to those in II is not feasible. In each case the two iron atoms could be *cis* or *trans* with respect to the ring. Initial nmr studies clearly indicated that the atoms are not disposed as in II, but the data were consistent with either formulation III or IV; this raised the question of possible bond fixation in the system. The implications of several X-ray studies of several iron tricarbonyl complexes containing aromatic ligands are now given.[4]

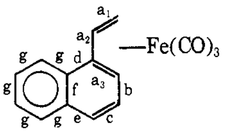
X-Ray analysis reveals the disposition of atoms in *p*-divinylbenzene–diiron hexacarbonyl,[3] *m*-divinylbenzene–diiron hexacarbonyl,[3] 1-vinylnaphthalene–iron tricarbonyl,[8] and 2-vinylnaphthalene–iron tricarbonyl[9] to be as indicated in formulas V–VIII, respectively. In the two diiron complexes the iron atoms are situated *trans* with respect to the ring. Bond distance data for these are summarized in Table I.



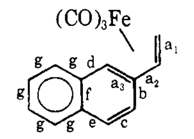
V



VI



VII



VIII

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(1) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4, 1314 (1965).

(2) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1298 (1965).

(3) T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 83, 3597 (1961).

(4) Structure refinements are complete for *p*-divinylbenzene–diiron hexacarbonyl (V), *m*-divinylbenzene–diiron hexacarbonyl (VI), 1-vinylnaphthalene–iron tricarbonyl (VII), 2-vinylnaphthalene–iron tricarbonyl (VIII), and carbomethoxybenzocyclobutadiene–iron tricarbonyl (X) (R = COO CH$_3$), with final *R* values of 0.052, 0.043, 0.044, 0.052, and 0.093, respectively. Estimated standard deviations for these bonds are in the range 0.01–0.02 Å. Manuscripts reporting details of the structure determinations, final atomic parameters, and molecular geometry are in preparation.[5–7] The degree of reliability of the bond distances in Table I may also be seen from the reproducibility of the 18 Fe—C and the 18 C═O values. For all structures, single crystal intensity data were collected by the stationary crystal–stationary counter method on a General Electric XRD-5 diffractometer, using balanced filter pairs. All structures were solved by the heavy atom method and refined by block diagonal least-squares calculations.

(5) R. E. Davis, in preparation.

(6) M. Jenks and R. E. Davis, in preparation.

(7) J. D. Oliver and R. E. Davis, in preparation.

(8) T. A. Manuel, *Inorg. Chem.*, 3, 1794 (1964).

(9) Prepared from 2-vinylnaphthalene and iron carbonyl.