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OXYGEN-INDUCED 1,4-ADDITION REACTION OF ORGANOBORANES TO CROTONALDIMINE

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Trialkylboranes undergo fast 1,4-addition to crotonaldimine in the presence of catalytic amounts of air to give, after methanolysis, the corresponding saturated aldimines in good yields. This reaction is considered to proceed through a radical process.

We have previously reported that trialkylboranes undergo a spontaneous 1,4-addition in the presence of oxygen to numerous α,β-unsaturated carbonyl compounds including methyl vinyl ketone,[1] methyl isopropenyl ketone,[2] acetylacetylene [3] and 1,3-butadiene monoxide,[4] 3,4-epoxy-1-butynes[5] and formaldehyde.[6] These reactions apparently proceed by a free-radical chain mechanism since they are promoted by typical free-radical initiators, and are inhibited by radical scavengers such as galvinoxyl.[2] We explored in an attempt to examine the possibility of achieving such a 1,4-addition reaction of organoboranes to α,β-unsaturated imine, which should provide a convenient synthetic procedure of aldimines.

No reaction occurs between N-isopropylcrotonaldimine and tri-n-butylborane in the absence of oxygen. However, the reaction proceeds smoothly by the introduction of small quantities of air (eq. 1).

$$R_3B + CH_3CH{=}CHCH{=}N\text{-}Pr^i \xrightarrow[2,\ CH_3OH]{1,\ O_2} RCHCH_2CH{=}N\text{-}Pr^i + R_2BOCH_3 \qquad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$$

The yield of the product imine increased proportionally with the amount of introduced oxygen, but an excess of oxygen decreases the yield. Indeed, quite satisfactory yields could be realized with 20-30% of oxygen. The results are shown in Table 1 for the reaction of tributylborane with N-isopropylcrotonaldimine.

Table 1. Oxygen Effect in the Reaction of Tri-n-butylborane with N-isopropylcrotonaldimine

Amount of oxygen (O_2/borane)	Yield of N-isopropyl-β-methyl-oenanthaldimine, %, based on n-Bu_3B
0.1	64
0.2	75
0.3	76
0.4	73
0.5	67
0.6	45

The product yield with an equimolar quantity of tri-n-butylborane and crotonaldimine was 33%. This was improved significantly by using an excess of the unsaturated aldimine. The representative results are summarized in Table 2. Both primary and secondary trialkylboranes react satisfactorily.

In this reaction, copper N,N-diethyldithiocarbamate was found to be an effective inhibitor. Consequently, the reaction seems to proceed through a free-radical chain process (eqs. 2-5), as seen in the reaction of organoboranes with α,β-unsaturated carbonyl compounds.[2,3] In all cases, better yields

Table 2. Reaction of Organoboranes with N-Isopropylcrotonaldimine in the Presence of Air

Organoborane R_3B	Molar ratio of aldimine (aldimine/R_3B)	Product[a] $RCH(CH_3)CH_2CH{=}N\text{-}Pr^i$	Yield, %[b]
Tri-n-propylborane	3	N-Isopropyl-β-methylcaproaldimine	69
Tri-n-butylborane	1	N-Isopropyl-β-methyloenanthaldimine	33
	3		76
Tri-n-pentylborane	3	N-Isopropyl-β-methylcapryladimine	83
Tricyclopentylborane	3	N-Isopropyl-β-cyclopentylbutyraldimine	53

a) All products were characterized by nmr and mass spectra, refractive index, and elemental analysis.

b) Based on the organoborane used.

were obtained when an excess of crotonaldimine and controlled oxygen minimized the destruction of the product.

$$R_3B + O_2 \longrightarrow R^{\cdot} \quad (2)$$

$$R^{\cdot} + CH_3CH{=}CHCH{=}N\text{-}Pr^i \longrightarrow \underset{\underline{1}}{RCH(CH_3)\text{-}CH\text{-}CH{=}N\text{-}Pr^i} \longleftrightarrow \underset{\underline{2}}{RCH(CH_3)\text{-}CH{=}CH\text{-}\dot{N}\text{-}Pr^i} \quad (3)$$

$$\underline{2} + R_3B \longrightarrow \underset{\underline{3}}{RCH(CH_3)CH{=}CH\text{-}N(BR_2)\text{-}Pr^i} + R^{\circ} \quad (4)$$

$$\underline{3} + CH_3OH \longrightarrow RCH(CH_3)CH_2CH{=}N\text{-}Pr^i + CH_3OBR_2 \quad (5)$$

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 charged a mixture of 0.333g (3 mmol) of N-isopropylcrotonaldimine[7] and 1 ml (1 mmol) of tri-n-butylborane in THF. Under stirring at 25°C, air was introduced into the flask at a rate of 1 ml/min through a syringe needle inserted into the septum cap to a point just above the reaction mixture. After 30 min, 1 ml of methanol was added and the mixture was stirred for 1 hr at room temperature. Analysis by glpc demonstrated that 0.76 mmol (76%) of N-isopropyl-β-methyl-oenanthaldimine had been formed.

REFERENCES

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.,72,710(1970).
3) A.Suzuki,S.Nozawa,M.Itoh,H.C.Brown,G.W.Kabalka,and G.W.Holland,ibid.,92,3503(1970).
4) A.Suzuki,N.Miyaura,M.Itoh,H.C.Brown,G.W.Holland,and E.Negishi,93,2792(1971).
5) A.Suzuki,N.Miyaura,M.Itoh,H.C.Brown,and P.Jacob,Synthesis,305(1973).
6) N.Miyaura,M.Itoh,A.Suzuki,H.C.Brown,M.M.Midland,and P.Jacob,J.Amer.Chem.Soc.,94,6549(1972).
7) R.Tiollais,Bull.Soc.Chim.France,14,708(1947).

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