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Preliminary communication

HYDRIDE-INDUCED CARBONYLATION OF ORGANOBORANES. EVIDENCE THAT ALL COMPLEX METAL HYDRIDES EVALUATED REACT BY WAY OF ALKALI METAL TRIALKYLBOROHYDRIDE INTERMEDIATES

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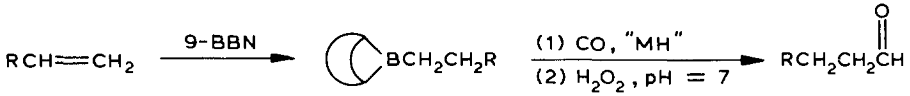
Summary

The hydride-induced carbonylation of organoboranes proceeds via alkali metal trialkylborohydride intermediates regardless of the complex metal hydride used. Apparent variations in alkyl group migratory aptitudes observed previously, which were attributed to differences in complex hydride steric requirements, evidently arise instead from selective formation of products that are difficult to oxidize.

Hydride-induced carbonylation is one of the most useful synthetic reactions of organoboranes. It provides a number of valuable transformations, including an approach for clean anti-Markovnikov hydroformylation of alkenes (eq. 1).



(1)

The reaction can be accomplished using a variety of complex metal hydrides, including lithium trimethoxyaluminohydride (LTMA) [1,2], lithium tri-t-butoxyaluminohydride (LTBA) [3], and potassium triisopropoxyborohydride (KIPBH) [4].

In spite of its utility, the reaction has presented some difficulty in terms of mechanistic understanding. Initially, it was proposed that the complex hydride

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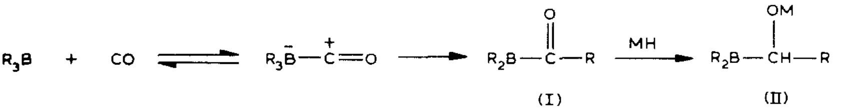
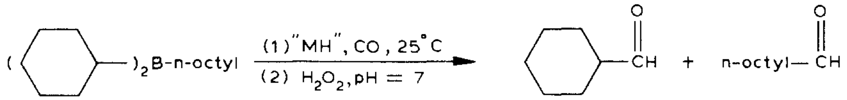


$$R_3B + CO \rightleftharpoons R_3\overset{-}{B}-\overset{+}{C}=O \longrightarrow \underset{(I)}{R_2B-\overset{O}{\overset{\|}{C}}-R} \xrightarrow{MH} \underset{(II)}{R_2B-\overset{OM}{\overset{|}{C}}H-R} \quad (2)$$

reduced an intermediate acylborane (I) formed by migration of one alkyl group from boron to carbon (eq. 2) [1]. The product, for which the structure II has been postulated, is then transformed to an aldehyde or other useful material [5,6].

Subsequently, a modified mechanism was proposed in response to results reported from carbonylation-oxidation of mixed organoboranes such as dicyclohexyl-n-octylborane. The proportions of cyclohexanecarboxaldehyde and

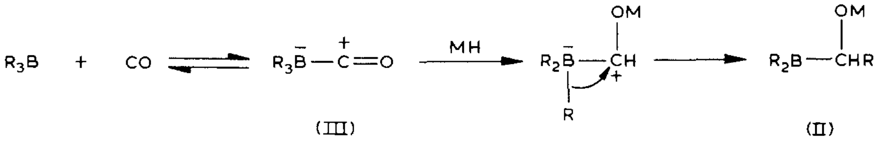


(3)

MH = LTMA 67/33

MH = LTBA 100/0

nonanal differed for LTMA and LTBA (eq. 3) [7], suggesting a difference in alkyl group migratory aptitudes based on the steric requirements of the added hydride. Thus, it was postulated that the complex hydride reduced the trialkylborane-carbon monoxide adduct (III) prior to its rearrangement (eq. 4).



$$R_3B + CO \rightleftharpoons \underset{(III)}{R_3\overset{-}{B}-\overset{+}{C}=O} \xrightarrow{MH} \underset{R}{\underset{|}{R_2\overset{-}{B}}}-\overset{OM}{\overset{|}{C}}H^{+} \longrightarrow \underset{(II)}{R_2B-\overset{OM}{\overset{|}{C}}HR} \quad (4)$$

However, it is now apparent that the complex hydrides used for carbonylation all transfer hydride to trialkylboranes to form trialkylborohydrides [8]. Furthermore, trialkylborohydrides themselves undergo carbonylation in the presence of catalytic quantities of free trialkylborane [9]. This evidence suggests that trialkylborohydrides, rather than the initially added complex hydrides, are the active reducing agents for III. Thus, alkyl group migration should be independent of complex hydride steric requirements.

In order to resolve this question, a detailed study of the carbonylation of mixed organoboranes in the presence of LTMA, LTBA, and KIPBH was undertaken. *B*-Alkyl-9-BBN derivatives and dialkylthexylboranes showed the same behavior with all three hydrides: migration of the alkyl group (for 9-BBN derivatives and di-n-alkylthexylboranes) or no reaction (for more hindered dialkylthexylboranes). However, the earlier results using dicyclohexyl-n-octylborane were reproduced, and results with KIPBH were similar to those with LTMA. Clearly, LTBA was the anomalous hydride.

The total yield of products from carbonylation-oxidation of dicyclohexyl-n-octylborane using LTBA was significantly lower than for the comparable reactions using the other hydrides. Indeed, although the proportion of cyclohexanecarboxaldehyde was substantially higher, the absolute yield [10] of this compound was comparable to that obtained with the other hydrides. This suggested that the anomalous result occurred because of failure to cleave boron from the product of n-octyl group migration in the LTBA reaction, a view supported by the presence of boron in the organic extract after oxidation. Evidently the relatively unhindered intermediate was transformed to a difficult-to-oxidize product; perhaps trimethoxyaluminum complexes with and stabilizes 2 in some way that the more sterically hindered tri-t-butoxyaluminum cannot. In order to test this possibility, the carbonylation of dicyclohexyl-n-octylborane in the presence of LTBA was investigated under varying conditions. The results are summarized in Table 1.

TABLE 1

PRODUCTS FROM CARBONYLATION OF DICYCLOHEXYL-n-OCTYLBORANE IN THE PRESENCE OF LTBA

Carbonylation conditions[a]	Pre-workup conditions[b]	Absolute yield (combined %)	Ratio $C_6H_{11}CHO/C_8H_{17}CHO$ (eq. 3)
25°C, 1 h	25°C, 1 h	65	98/2
<–25°C, 2 h	–20°C, 30 min	35	77/23
<–20°C, 3 h	<–20°C, 5 min	73	55/45
	>30°C, 30 min	38	92/8

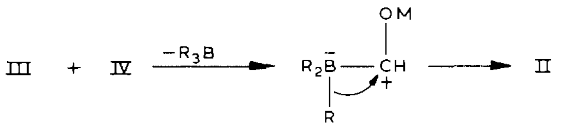
[a] Conditions maintained during reaction of the hydride, carbon monoxide, and organoborane. [b] Conditions maintained while the reaction vessel was being flushed with nitrogen and left to stand prior to addition of the oxidizing mixture.

At ambient temperature the product was almost entirely cyclohexanecarboxaldehyde, in a yield of 65%. At lower temperatures the absorption of carbon monoxide was relatively slow and yields were low unless longer reaction times were employed. However, there was a significant increase in the proportion of nonanal, the minor component at ambient temperature. This is the opposite of expectations for a product distribution reflecting the selectivity of migration, but is consistent with greater stability of an unstable intermediate at the lower temperature. That this is indeed the explanation is strongly indicated by the final entry in the Table, representing a reaction mixture which was divided into equal parts after carbonylation at –20°C. The portion which was oxidized immediately, without warming, gave a good yield and a high proportion of nonanal. The portion which was warmed gently for thirty minutes prior to oxidation gave a much lower yield, almost entirely as a result of the disappearance of nonanal.

Clearly, in the presence of tri-t-butoxyaluminum (or something else present during the reaction involving LTBA) the organoborane carbonylation intermediates, especially those arising from primary alkyl group migration, are unstable and are transformed into material (perhaps a polymer) which is difficult to oxidize. The apparent differences in alkyl group migratory aptitudes observed when LTBA is the hydride source result only because carbonylation intermediates arising from migration of relatively unhindered alkyl groups are rapidly transformed into material which resists oxidation. Consequently, the only objection to the intermediacy of a common reducing agent, trialkylborohydride, is now removed.

$$R_3B + MXH \longrightarrow \underset{(IV)}{MR_3BH} + X \qquad (MH = LTMA/LTBA/KIPBH) \qquad (5)$$

$$R_3B + CO \rightleftharpoons III \qquad (6)$$



$$III + IV \xrightarrow{-R_3B} \underset{R}{\underset{|}{R_2\bar{B}}}-\overset{OM}{\overset{|}{C}}H^{+} \longrightarrow II \qquad (7)$$

Thus, the actual mechanism of the hydride-induced carbonylation of organoboranes appears to be as outlined in eq. 5—7. The trialkylborane regenerated in the last step is recycled (eq. 5 and 6) until all the hydride is consumed. This postulated mechanism is quite similar to that proposed for carbonylation of alkali metal trialkylborohydrides [9]. Therefore, it is probable that carbonylation occurs only in the presence of a catalytic quantity of free trialkylborane. The reaction rate may be retarded considerably when an excess of the complex hydride is used, particularly in the case of KIPBH.

Of considerable interest is the actual nature of the product for which structure II has been proposed. There is substantial evidence that II is not the correct constitution; e.g., ^{11}B NMR indicates the boron may be tetracoordinate. Efforts to clarify the structure of this versatile material are the subject of continuing investigation.

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References and Notes

1 H.C. Brown, R.A. Coleman and M.W. Rathke, J. Am. Chem. Soc., 90 (1968) 499.
2 H.C. Brown, E.F. Knights and R.A. Coleman, J. Am. Chem. Soc., 91 (1969) 2144.
3 H.C. Brown and R.A. Coleman, J. Am. Chem. Soc., 91 (1969) 4606.
4 H.C. Brown, J.L. Hubbard and K. Smith, Synthesis, (1979) 701.
5 J.L. Hubbard and H.C. Brown, Synthesis, (1978) 676.
6 H.C. Brown, T.M. Ford and J.L. Hubbard, J. Org. Chem., 45 (1980) 4067.
7 R.A. Coleman, Ph.D. Thesis, Purdue University, 1970.
8 (a) H.C. Brown, S. Krishnamurthy and J.L. Hubbard, J. Organomet. Chem., 166 (1979) 271; (b) H.C. Brown, S. Krishnamurthy, R.A. Coleman and J.L. Hubbard, ibid., 166 (1979) 281; (c) C.A. Brown and J.L. Hubbard, J. Am. Chem. Soc., 101 (1979) 3964.
9 H.C. Brown and J.L. Hubbard, J. Org. Chem., 44 (1979) 467.
10 Absolute yields are determined by GLC using an internal standard and carefully measured detector response ratios.