

Preliminary communication

REMARKABLE COUNTERCATION EFFECT IN THE REACTION OF ORGANOBORANES WITH ENOLATES

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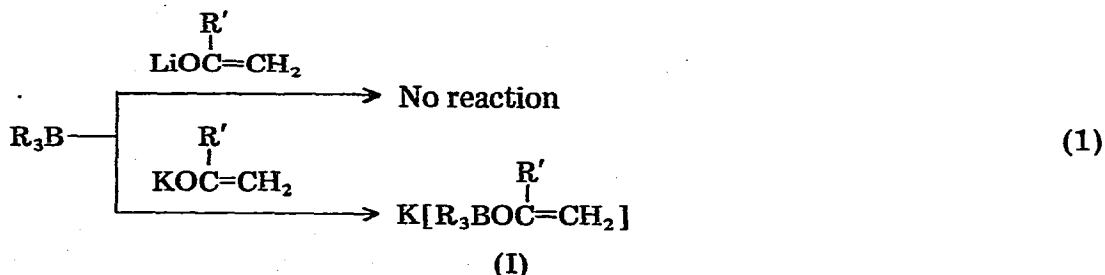
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Summary

^1H and ^{11}B NMR evidence that, whereas lithium enolates derived from ketones do not detectably interact with triorganoboranes, the corresponding potassium enolates react with relatively unhindered triorganoboranes to form potassium enoxyborates often without any indication of dissociation is presented.

Metal organoborates have recently emerged as unique intermediates and reagents in organic synthesis [1]. In the past, the metal component in these organoborates has mostly been restricted to lithium, and relatively little has been known about the countercation effect. In an attempt to moderate the reactivity of enolates, we treated lithium enolates derived from several ketones, e.g., acetophenone, with typical triorganoboranes, e.g., triethylborane, and observed virtually no reaction [2].

We now present the first clear-cut NMR evidence that, in sharp contrast with lithium enolates derived from ketones, the corresponding potassium enolates do react with triorganoboranes to form potassium enoxyborates (I) often without showing any indication of dissociation (eq. 1).

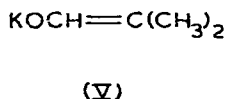
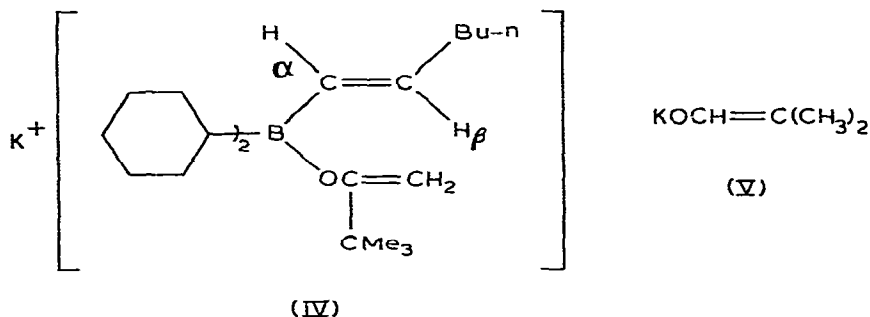
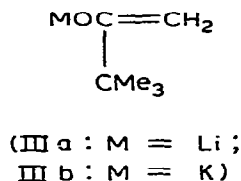
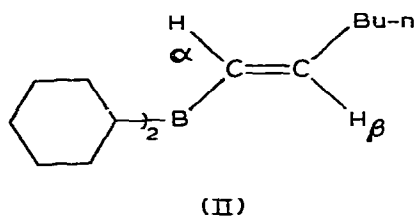


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We recently became aware of a dramatic difference between lithium and potassium in the "borane-moderated" reaction of enolates with alkyl halides [3]. In view of the potential synthetic significance of such a counteraction effect we hoped to clarify its origin and undertook a ^1H and ^{11}B NMR study of the reaction of lithium and potassium enolates with organoboranes.

The first quantitative spectroscopic observations indicating the nature of the difference between lithium and potassium were made in our ^1H NMR examination of the reaction of (*E*)-1-hexenyldicyclohexylborane (II) with metal enolates derived from pinacolone (III).

The ^1H NMR spectrum of a 1/1 mixture of II and IIIa ($\text{M} = \text{Li}$) in tetrahydrofuran (THF) shows the olefinic α and β protons at δ 6.16 (d, J 18 Hz) and 6.76 (d of t, J 18 and 6 Hz) ppm, respectively. These values are virtually identical with those for II alone in THF.



No olefinic proton peaks are discernible in the 5.0–6.0 ppm region where the more highly shielded alkenyl protons of alkenylborates have been observed in other instances [2]. On the other hand, the ^1H NMR spectra of a 1/1 mixture of II and the potassium enolate (IIIb) derived from pinacolone and KH [4] shows two sets of signals for the α and β protons at δ 5.90 (d, J 18 Hz) and 5.30 (d of t, J 18 and 6 Hz) ppm, respectively. Significantly, when an additional amount of II is added to the above reaction mixture, both the olefinic product in the mixture and II maintain the same spectral features as described above. These results clearly indicate that the reaction of II and IIIb proceeds to completion to form the corresponding potassium enoxyborate (IV) and that the alkenyloxy exchange between II and IV, if it all, is slow on the NMR time scale. Essentially the same chemical shift values have also been observed for the reaction of II with the potassium enolate derived from acetophenone.

To rule out special effects, if any, associated with II, we have examined the reaction of III with more typical triorganoboranes, e.g., Et_3B and $s\text{-Bu}_3\text{B}$ by ^{11}B NMR. As expected, the ^{11}B NMR spectrum of a 1/1 mixture of IIIb and Et_3B shows only one peak at 2.0 ppm* without showing a peak for free Et_3B , while the spectrum of a 1/1 mixture of IIIa and Et_3B shows only the peak for Et_3B at -76.4 ppm [5]. Interestingly, addition of one equivalent of LiBr to the 1/1 mixture of IIIb and Et_3B shifts the boron signal from -2.0 ppm to -76.4 ppm. This effect of LiBr has been observed in several other cases as well.

The equilibrium constant for the formation of enoxyborates is, of course, a function of various other factors as well. Thus the reaction of IIIb with $i\text{-Bu}_3\text{B}$ or $s\text{-Bu}_3\text{B}$ proceeds only to the extent of $< 10\text{--}20\%$, as judged by ^{11}B NMR. On the other hand, the potassium enolate derived from isobutyraldehyde (V) reacts with Et_3B ($>99\%$), $i\text{-Bu}_3\text{B}$ ($>99\%$) and $s\text{-Bu}_3\text{B}$ ($>95\%$) to form the corresponding enoxyborates, the extent of complexation being indicated in parentheses. Furthermore, even the corresponding lithium enolate undergoes a nearly complete ($>95\%$) complexation with unhindered organoboranes, e.g., Et_3B .

The spectroscopic data herein reported have unequivocally established, for the first time, the formation of metal enoxytriorganoborates. They also nicely account for the marked counteraction effect in the "borane-moderated" alkylation reaction of enolates. Perhaps more importantly, the realization of the marked counteraction effect in the organoborate formation via organoborane-organometal complexation should prove generally useful in expanding the scope and synthetic utility of chemistry of organoborates.

References

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*These values are relative to external $\text{BF}_3 \cdot \text{OEt}_2$.