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THE DIMESITYLBORON GROUP IN ORGANIC SYNTHESIS, X. STUDIES ON THE THERMAL ISOMERISATION OF DIARYL-3-HEXYLBORANES

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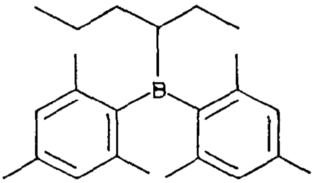
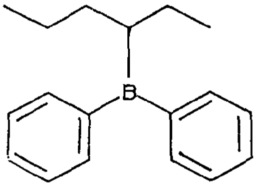
Summary: Dimesityl-3-hexylborane is unexpectedly resistant to isomerisation as compared with diphenyl-3-hexylborane. A possible explanation is proposed. Inorganic salts may profoundly affect the rate of isomerisation of diarylalkylboranes.

The thermal isomerisation of trialkylboranes is well known[1] and presents both significant opportunities and problems in organic synthesis. In particular, it has been used for the functionalisation of unactivated primary carbon atoms[2]. The reaction mainly proceeds by a retrohydroboration-hydroboration sequence[3] (but see ref. 4 for alternative mechanism) and the factors affecting the ease of migration have been studied. Specifically, the ease of isomerisation of dialkyl-3-hexylboranes in diglyme at 150°C has been assessed and it has been proposed that the more bulky the alkyl groups, the more ready the migration[5,6]. This effect has been attributed to the greater relief of steric strain associated with the release of the more bulky dialkylborane in the rate-limiting retrohydroboration step.

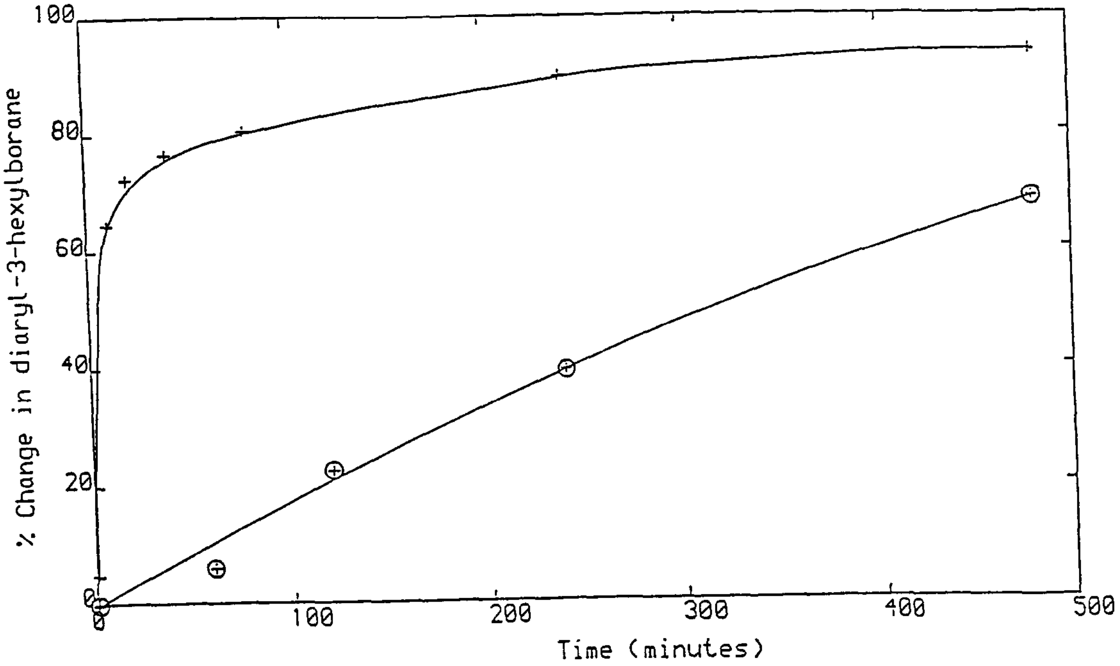


(1)



(2)

In our studies of the alkylation of carbanions α to a dimesitylboron group[7] it was of paramount importance to know whether the alkylated product retained its regiochemical integrity or whether the very bulky dimesitylboron group migrated readily along the chain formed by alkylation. If the latter had happened the utility of the process would be vitiated. To our pleasure, initial studies[8] indicated that 2- and 3-alkyldimesitylboranes were compounds of great stability, in contrast to expectations based on previous work. This welcome result was so unexpected that we initiated studies to compare the rates of isomerisation of dimesityl-3-hexylborane, (1) and diphenyl-3-hexylborane, (2), under conditions directly comparable with those used in the isomerisation studies of dialkyl-3-hexylboranes[5,6]. The results with highly purified boranes are shown in the Figure and Table.



⊕ = dimesityl-3-hexylborane (1), + = diphenyl-3-hexylborane(2).

FIGURE. Comparison of the rate of isomerisation of 1 and 2 at 150°C in diglyme.

Not shown are experiments involving the heating of (1) at 100°C and 120°C, as in both cases no isomerisation was noted even after 6 h heating. At 150°C, (1) isomerised to the extent of 68% after 8 h. In addition to the slow rate observed, two other points of interest emerged. Firstly, there was no isomerisation to the unhindered primary position. This was not due to preferential destruction of dimesityl-1-hexylborane (3), as when an authentic sample of (3) was subjected to the same conditions (Table), it was neither isomerised nor destroyed. Secondly, the isomerisation of (1) is accompanied by an overall destruction of any dimesitylhexylboranes present, in a fashion unlike that of dialkylhexylboranes. When compound (2) was subjected to the same conditions, isomerisation

TABLE

Isomerisation of diarylhexylboranes at 150°C in diglyme

Time (min)	(**1**) 3-ol,	(**1**) 2-ol,	(**1**) 1-ol[a]	(**1**) % Total Yield[b]	(**2**) 3-ol,	(**2**) 2-ol,	(**2**) 1-ol	(**2**) % Total Yield	(**3**) 3-ol,	(**3**) 2-ol,	(**3**) 1-ol	(**3**) % Total Yield
0	100	0	0	100	95	5	0	100	0	0	100	100
10	-	-	-	-	35	65	0	92	0	0	99	99
20	-	-	-	-	28	59	13	98	0	0	97	97
40	-	-	-	-	23	51	26	100	0	0	100	100
60	94	6	0	57	-	-	-	-	-	-	-	-
80	-	-	-	-	20	41	40	100	-	-	-	-
120	78	22	0	33	-	-	-	-	0	0	100	100
240	61	39	0	25	10	17	73	83	-	-	-	-
480	32	68	0	17	6	8	86	54	-	-	-	-

[a] Refers to hexan-1-ol, hexan-2-ol, hexan-3-ol in each case, the yields being normalised.

[b] This is the absolute amount of diarylhexylboranes present, compared with initial amount as 100%.

was 80% complete in about 1 h* and, in that time there was little destruction of organoboranes. Thus the very large increase in steric hindrance associated with dimesityl-3-hexylborane as compared with diphenyl-3-hexylborane had led to a <u>decrease</u> in the rate of isomerisation, in direct contrast to previous results with dialkyl-3-hexylboranes.

We propose that possibly the slowness of the isomerisation of (**1**) indicates a change of the rate-limiting step of the isomerisation from the retrohydroboration to the hydroboration step. We have shown previously[9] that internal alkenes are hydroborated by dimesitylborane only with difficulty, in contrast with the rapid hydroboration of alkenes by diphenylborane[10]. In this connection, it is of interest that nonenes were present when dimesityl-3-nonylborane was heated for 3 h at 150°C in diglyme. This proposal also explains the unusual loss of yield on heating (**1**), as, unlike diphenylborane, the dimesitylborane formed may exist long enough to undergo alternate decomposition.

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* We thank U.S. Racherla and H.C. Brown for informing us of a similar result.

Unless highly purified diaryl-3-hexylboranes were used, there was difficulty in the reproduction of results, a problem traced to the presence of salts. Thus addition of one molar equivalent of either lithium or sodium methoxide to the solution totally inhibited the isomerisation of (**1**) and also lowered the amount of decomposition. Sodium bromide had no effect[*]. Very strikingly the ready isomerisation of (**2**) is completely inhibited by the presence of lithium methoxide or magnesium bromide. Presumably this inhibition is due to ate complex formation.

These results demand that caution be exercised in the interpretation of studies of the thermal isomerisation of organoboranes which at any time have been in contact with salts. They also point the way to the stabilisation of organoboranes for synthetic usage.

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[*] We thank U.S. Racherla for informing us that 5% LiF, LiCl and LiBr also inhibit the isomerisation of (**1**).

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