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THE DIMESITYLBORON GROUP IN ORGANIC SYNTHESIS. 4. THE 'BORON WITTIG' REACTION

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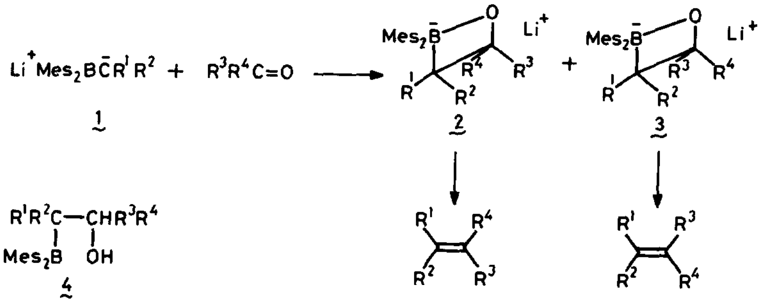
Anions generated α- to a dimesitylboron group readily condense with aldehydes and ketones. Elimination of Mes_2BOLi then leads to alkenes in a boron analogue of the Wittig reaction.

The first anion produced by deprotonation of an organoborane was derived from 9-methyl-9-BBN.[1] Part proof of its production was to quench with cyclohexanone which led in reasonable yields to methylenecyclohexane in a reaction closely analogous to the Wittig reaction. We felt that, given the considerably shorter bond lengths of B-O and C-O[2] as compared with the corresponding bond lengths of any other metalloid, then the transition states leading to the cyclic borate complexes 2 and 3 (Scheme) should be particularly sensitive to steric effects and that therefore the reactions should be particularly stereoselective. As we can readily produce anions 1, stabilised by an adjacent dimesityl boron group,[3] we decided to investigate the reactions of these anions with aldehydes and ketones to see whether we could synthesise alkenes by a 'boron-Wittig' reaction.

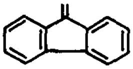
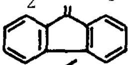
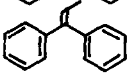
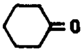
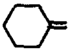


We first examined benzophenone as an example of a non-enolisable ketone of reasonable bulk. The reaction of 1 ($R^1 = R^2 = H$) with this ketone in THF at 25°C was instantaneous and after chromatography a 75% yield of 1, 1-diphenylethene 5 was isolated. From the column a small quantity (6%) of alcohol 4 ($R^1 = R^2 = H$, $R^3 = R^4 = Ph$) was also isolated. This was converted to 5 simply by warming in chloroform. We sometimes found that lithium salts, presumably corresponding to 2/3 separated from the reactions as crystalline solids and that solution in chloroform (and sometimes warming) was sufficient to induce elimination to the desired alkenes. Our results are presented in the Table.

Having found that benzophenone condenses with 1, $R^1 = R^2 = H$, (Table, exp. 1) we decided to test whether increasing steric hindrance inhibited the reaction. We were pleased to find that anions 1 ($R^1 = H$, $R^2 = Me$ and $R^1 = H$, $R^2 = Hept$) yield the corresponding alkenes in good yields (Table, exp. 2,3). Fluorenone gives the corresponding dibenzofulvenes (Table exp. 4,5) in good yields, a testimony to the gentleness of the procedure, as these alkenes readily polymerise.

Table

'Boron-Wittig' reactions of anions derived from Mes_2BR

Experiment	Ketone/Aldehyde	R of Mes_2BR	Akene Product[a]	Temp.°C	% Yield
1	Ph_2CO	Me	$Ph_2C{:}CH_2$	25	95(75)
2	Ph_2CO	Et	$Ph_2C{:}CHMe$	0	99(70)
3	Ph_2CO	Oct	$Ph_2C{:}CHHept$	0	90(70)
4		Me		25	(80)
5	"	Et		0	(90)
6	PhCHO	Oct	PhCH:CH.Hept[c]	0	60(40)[d]
7	Hept.CHO	Me	$Hept.CH{:}CH_2$	25	20
8	Hept.CHO	Me	$Hept.CH{:}CH_2$	-78	80
9		Me		25	30
10	"	Me	"	-78	70

a) All alkenes fully characterised or compared directly with authentic samples.

b) yields are g.c. estimates except those in brackets which are yields of isolated, purified products. c) At least 99.9% trans-isomer. d) An additional 40% of $PhCHOHCH_2Hept$ isolated.

The reaction of benzaldehyde (Table.exp 6) with the anion from octyldimesitylborane is of particular interest as it is the first reaction which can give an indication of the stereoselectivity of the reaction. Mixing the components gave a salt that was stable in chloroform for 24h. at 25°C, unlike the salt derived from the same anion (Table, exp.3) and benzophenone which rapidly decomposed on solution in chloroform at 25°C. The benzaldehyde product was therefore refluxed for two hours in chloroform and the products separated by chromatography. The first fractions gave 1-phenylnon-1-ene (40%) that was 99.9% trans!! Hence alkene production is essentially stereospecific. However we were puzzled by the low yield and continued elution, so isolating 40% of 1-phenylnonanol (Table, exp. 6, Note d). The production of this alcohol is strange as it involves a cleavage of the B-alkyl bond of an alkyldimesitylborane in extraordinarily mild conditions. In general we find this a difficult process and hence are forced to invoke an interesting neighbouring group effect in the present instance.

At room temperature the reactions with enolisable ketons and aldehydes proceed poorly (Table, exp. 7,9) suggesting that anion exchange competes well with condensation. At -78°C however, the reaction proceeded in good yield, possibly via a different mechanism.

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References

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2. Tables of Interatomic Distances and Configuration in Molecules and Ions, Chem.Soc. Special Publication No. 11, 1958, Supplement. Special Publication No. 18, 1965.
3. See Parts 1 and 2 of this series.

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