Novel Double Migration in the Reaction of Trialkylalkynylborates with Dihalogenomethanes

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Summary Trialkylalkynylborates react readily with some dihalogenomethanes undergoing two alkyl migrations to give, after hydrolysis, good yields of terminal olefins.

Alkylation reactions of trialkylalkynylborates (I) have recently proved to be versatile routes to a wide range of olefins and ketones.[1] In the alkylations examined so far only one group migrates from boron to the neighbouring alkynyl carbon atom whereas acylation may induce two migrations under certain conditions[2] although the double migration product is obtained in only moderate yield.

Table

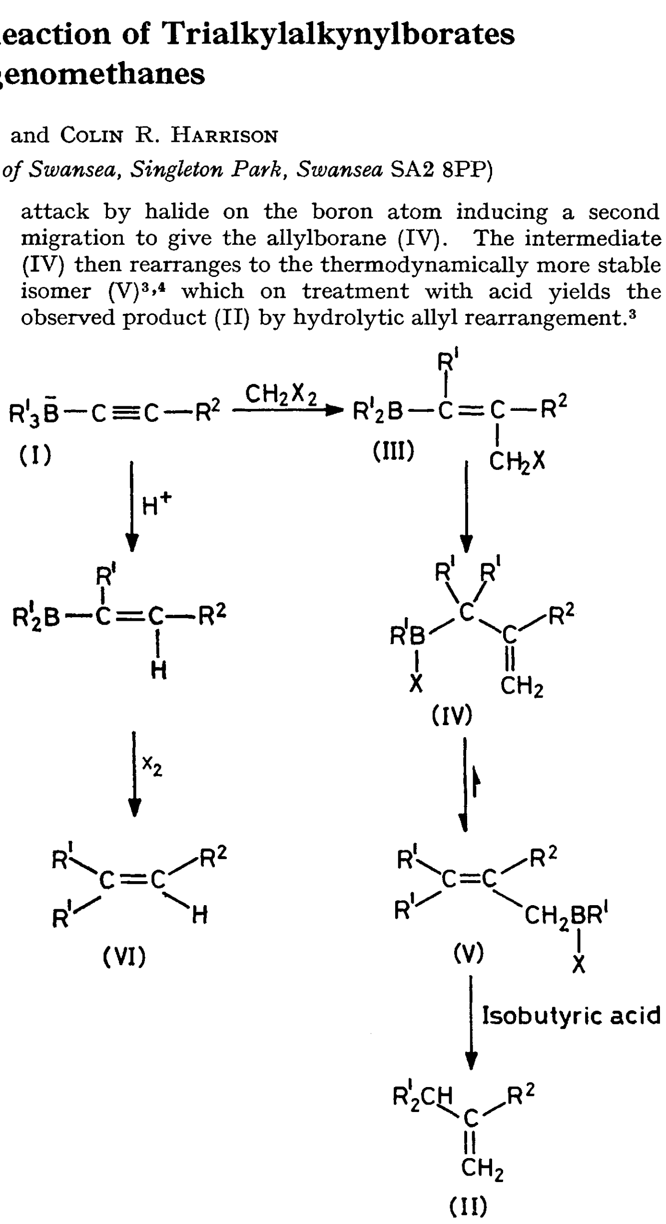
Synthesis of $CH_2{=}CR^2{\cdot}CHR^1_2$ from $R^1_3\bar{B}{-}C{\equiv}C{-}R^2$ and CH_2X_2

R^1	R^2	X	Time/ h	Temp./ °C	Yield of (II)[a] (%)
n-Hexyl	Bu^n	Br	12	55	74 (7)
n-Octyl	n-Hexyl	"	"	"	71 (6)
Cyclopentyl	"	"	"	70	68
n-Hexyl	Bu^n	I	5	50	65 (10)
n-Octyl	n-Hexyl	"	"	"	58 (8)
Cyclopentyl	"	"	10	"	50

[a] Yield of isolated (II) corrected for the presence of (VI), where appropriate, by g.l.c. using an internal standard and response factors calculated from pure (II) and (VI). Figure in parentheses is yield of (VI) by g.l.c. All new compounds gave satisfactory elemental analyses.

We here report the first double alkyl migration induced by alkylation of trialkylalkynylborates. We were interested in the reactions of bifunctional alkylating agents with lithium trialkylalkynylborates and studied di-iodomethane and dibromomethane. The salts (I) were prepared in diglyme, treated with the dihalogenomethane at 0° and warmed to complete the reaction; subsequent hydrolysis with isobutyric acid followed by acetate-buffered hydrogen peroxide oxidation yielded a hydrocarbon product. We were surprised to find that this was the olefin (II) formed by the transfer of two alkyl groups from boron to carbon presumably *via* the processes indicated in the Scheme.

Initial attack of the dihalogenomethane on (I) leads to formation of the alkenylborane (III) through one migration. This is followed by intramolecular or possibly intermolecular attack by halide on the boron atom inducing a second migration to give the allylborane (IV). The intermediate (IV) then rearranges to the thermodynamically more stable isomer (V)[3,4] which on treatment with acid yields the observed product (II) by hydrolytic allyl rearrangement.[3]



The best yields of the terminal olefins (II) were obtained using dibromomethane rather than di-iodomethane (Table) although the lower reactivity of the dibromo-compound necessitates the use of higher temperature to complete the reaction. Both primary and secondary groups migrate readily but in the case of primary groups small amounts of a byproduct postulated to be the olefin (VI) were isolated. The compound (VI) could arise by initial protonation and one migration[1] followed by attack of free halogen, formed by disproportionation of the dihalide, inducing a second migration and subsequent elimination[5] (Scheme). To test this hypothesis the borate (I) was treated successively with acid and then with iodine when the olefin (VI) was obtained in 65% yield. Careful purification of the dihalides to remove acidic impurities minimised the yield of the unwanted by-product (VI).

As well as being the first example of a double alkyl transfer from trialkylalkynylborates induced by alkylation this reaction provides a completely new route to the allylborane systems (V) and gives an extremely convenient synthesis of the highly branched olefins (II).

Extension of the reaction to other *gem*-dihalides is currently under investigation as is the oxidation of the allylboranes (V).

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