

Preliminary communication

THE ADDITION OF METHYLBORYLENE TO ACETYLENES

S.M. VAN DER KERK, A.L.M. VAN EEKEREN, and G.J.M. VAN DER KERK

Laboratory for Organic Chemistry, State University of Utrecht, Croesestraat 79, Utrecht (The Netherlands)

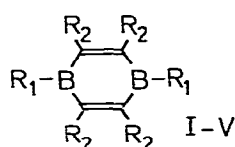
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Summary

The synthesis of alkyl-substituted 1,4-dimethyl-1,4-diboracyclohexa-2,5-dienes from dialkylacetylenes and the system $C_8K/MeBBr_2$ is described.

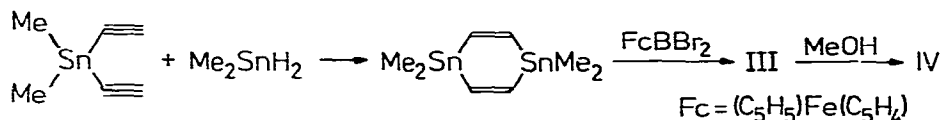
We report the synthesis of 1,4-dimethyl-2,3,5,6-tetra-*n*-butyl-1,4-diboracyclohexa-2,5-diene (I) via the addition of methylborylene, $MeB:$, to 5-decyne.

Derivatives of the 1,4-diboracyclohexa-2,5-diene system have been synthesized by Timms (II) [1,2] and by Herberich (III, IV) [3,4].



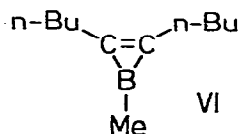
- I $R_1=Me$; $R_2=n-Bu$
 II $R_1=F$; $R_2=H, Me$
 III $R_1=(C_5H_5)Fe(C_5H_4)$; $R_2=H$
 IV $R_1=OMe$; $R_2=H$
 V $R_1=R_2=Ph$

Timms obtained compounds II by cocondensation of boron monofluoride, BF_3 , with acetylenes at liquid nitrogen temperature; Herberich and Hessner devised the following route to III and IV:



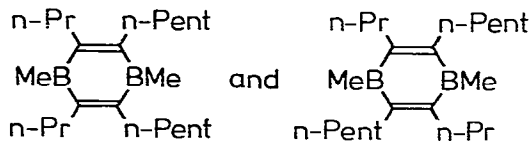
Joy, Lappert, and Prokai [5] claimed the synthesis of hexaphenyl-1,4-diboracyclohexa-2,5-diene (V), via a presumed borylene mechanism: phenylboron dibromide was added to a mixture of diphenylacetylene and potassium metal in boiling petroleum ether to yield V. However, Eisch was not able to reproduce their results [6], and neither could Lappert's group do so later [6].

In our work the borylene was generated by adding methylboron dibromide slowly to C_8K in boiling benzene [7]. Initially diphenylacetylene was used, but, in agreement with Eisch, we could not isolate the expected 1,4-diboracyclohexa-2,5-diene derivative or detect it by GC/MS. When, however, 5-decyne was used as a capturing agent, compound I was obtained by vacuum distillation of the product mixture (b.p. of I: $90-100^\circ C/10^{-5}$ mmHg), as an air-sensitive, viscous, yellow liquid. Some hexa-*n*-butylbenzene was also isolated. No trace of the other product which might be expected in this reaction, viz. 1-methyl-2,3-di-*n*-butyl-1-boracyclopropene (VI), was detected. (The products were identified by proton NMR and GC/MS.)



The mass spectrum of I (parent peak m/e 328) indicated the presence of two boron atoms in one molecule: the intensity ratio of the peaks 326, 327, and 328 was 1/8/16 (the natural abundance ratio of ^{10}B and ^{11}B being 1/4).

The formation of a 1,4-diboracyclohexa-2,5-diene derivative was confirmed by carrying out the borylene addition reaction with 4-decyne [(*n*-propyl)(*n*-pentyl)acetylene]. GC/MS examination of the products showed two peaks having almost the same retention times, the same parent peaks (m/e 326, 327, 328, with intensity ratio 1/8/16), and very similar mass spectra appeared. The following two isomers had apparently been formed:

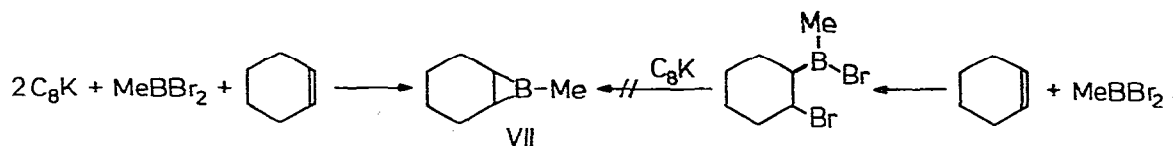


1,3,5-Tri-*n*-propyl-2,4,6-tri-*n*-pentylbenzene was also identified in the products.

Woodward and his coworkers synthesized transition metal sandwich complexes of II [8,9] by irradiation of a mixture of II and metal carbonyls in toluene. They obtained (among other products) $(C_4Me_4B_2)Ni(CO)_2$, $(C_4Me_4B_2F_2)_2Ni$, and $(C_4Me_4B_2F_2)Fe(CO)_3$. Irradiation of a mixture of I and iron pentacarbonyl in *n*-hexane yielded a deep red solution and a precipitate of iron enneacarbonyl; but the soluble red compound decomposed on sublimation. We assume, on grounds to be published later, that the addition of methylborylene to olefinic [7] or acetylenic systems proceeds via a free borylene mechanism.

The doubts cast by Eisch and Becker [6] upon our earlier work [7] are in our opinion unjustified. They stated that the apparent addition of methylborylene to cyclohexene was in fact the result of haloboration of the olefin, subsequent elimination of the bromine atoms by C_8K , and ring closure. Prolonged

treatment of cyclohexene with an equivalent amount of methylboron dibromide in boiling benzene yielded a product, which according to Eisch and Becker [6] is the haloboration product 1-bromo-2-(methylbromo)boronycyclohexane. However, after removal of unreacted cyclohexene and methylboron dibromide, the residue upon treatment with C_8K did not produce any 7-methyl-7-borabicyclo-[4.1.0]heptane (VII) (GC/MS). On the other hand, the same procedure with C_8K present produced VII, as previously reported [7].



Acknowledgement

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