Synthesis of Symmetrical Diynes *via* Reaction of Lithium Dialkyldialkynylborates with Iodine

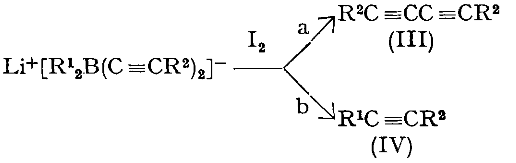
By ANDREW PELTER,* KEITH SMITH, and MASAYOSHI TABATA
(*Department of Chemistry, University College of Swansea, Singleton Park, Swansea* SA2 8PP)

Summary Low-temperature reaction of lithium dialkyldialkynylborates $Li^+[R^1_2B(C{\equiv}CR^2)_2]^-$ (R^1 = 1,2-dimethylpropyl or cyclohexyl) with iodine in tetrahydrofuran gives symmetrical conjugated diynes in excellent yield.

As a preliminary to an extensive investigation of borate complexes containing more than one unsaturated group we have studied the iodination–elimination of dialkyldialkynylborates (II), which are prepared in essentially quantitative yield by reaction (1).[1]

$$\underset{\text{(I)}}{R^1_2BX} + 2LiC{\equiv}CR^2 \longrightarrow \underset{\text{(II)}}{Li^+[R^1_2B(C{\equiv}CR^2)_2]^-} + LiX \qquad (1)$$

It is known that the reaction of iodine at low temperatures with trialkylalkynylborates is an excellent method for the preparation of disubstituted alkynes (IV).[2] The migration of an alkyl group from the salts (II) was therefore a possible competitor [reaction (2b)] with the desired migration of an alkynyl group to give the product (III) [reaction (2a)]. Hence an alkyl group R^1 which had a low migratory atpitude had to be found so that reaction (2b) should be suppressed relative to (2a).



(2)

Initial studies indicated that primary alkyl groups were unsuitable for this purpose and somewhat surprisingly the use of 9-chloro- or 9-methoxy-9-borabicyclo[3,3,1]nonane[3] was also fruitless. However bromodicyclohexylborane[4] or chlorobis-(1,2-dimethylpropyl)borane† led to salts (II) which on reaction with iodine gave overwhelmingly the required diynes (III). The use of chlorobis-(1,2-dimethylpropyl)borane led to slightly cleaner products but bromodicyclohexylborane was particularly simple to prepare in pure form on a large scale by a method we have recently developed.[4] The choice between the two reagents will depend therefore on factors, particularly the ease of separation of (III) from traces of (IV), which will have to be assessed for each specific reaction.

The 'one-pot' reactions were carried out by first treating the dialkylhalogenoboranes (I) with the appropriate alkynyl-lithium in tetrahydrofuran to give the salts (II). Without isolation these were cooled to −78 °C and treated with 1 equiv. of iodine. The reaction mixture was allowed to warm to 0 °C and quenched with $Na_2S_2O_3$ solution. The diyne was either isolated or estimated by g.l.c. using an internal standard. The results are presented in the Table.

TABLE

Preparation of symmetrical diynes $R^2C{\equiv}C{\cdot}C{\equiv}R^2$ (III)

Halogenoborane (I)	R^2	Yield of diyne (III) %[a]
Bromodicyclohexylborane	Bu^n	90
"	n-Octyl	72
"	Bu^t	92
$(Me_2CHCHMe)_2BCl$	Bu^n	(91)
"	n-Hexyl	85
"	n-Octyl	77
"	Bu^t	(96)
"	Ph	72 (69)

[a] Yields were estimated by g.l.c. except those in parentheses which are isolated yields of purified product. All products have been completely characterised.

The reaction is another in the series in which conjugated organic systems may be produced by means of borate intermediates.[5] It represents a completely new approach to the coupling of alkynes, one that proceeds in good yield and in such mild conditions that many functional groups should be accommodated. It appears to be general and if our current attempts to prepare the unsymmetrical salts $[R^1_2B(C \equiv CR^2)(C \equiv CR^3)]^-$ in high yield are successful, the reaction should provide direct access to unsymmetrical conjugated diynes without the requirement for the preparation of bromoalkynes.[6]

One of us (M.T.) thanks the S.R.C. for a maintenance award during the progress of this work.

(*Received, 5th September* 1975; *Com.* 1008.)

---

† Prepared by treatment of $(Me_2CHCHMe)_2BH$ with anhydrous HCl in tetrahydrofuran.

[1] P. Binger, G. Benedikt, G. W. Rotermund, and R. Köster, *Annalen*, 1968, **717**, 21.
[2] A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair, and M. M. Midland, *J. Amer. Chem. Soc.*, 1973, **95**, 3080; M. M. Midland, J. A. Sinclair, and H. C. Brown, *J. Org. Chem.*, 1974, **39**, 731.
[3] G. W. Kramer and H. C. Brown, *J. Organometallic Chem.*, 1974, **73**, 1.
[4] A. Pelter, K. Rowe, D. N. Sharrocks, and K. Smith, *J.C.S. Chem. Comm.*, 1975, 531.
[5] E. Negishi and T. Yoshida, *J.C.S. Chem. Comm.*, 1973, 606; E. Negishi, G. Lew, and T. Yoshida, *ibid.*, p. 874.
[6] W. Chodkiewicz, *Ann. Chim.*, 1957, **2**, 819; J. Rauss, P. Cadiot, and A. Willemart, *Compt. rend.*, 1960, **250**, 558.