A Highly Stereoselective and General Synthesis of Conjugated *trans,trans*-Dienes and *trans*-Alkyl Ketones *via* Hydroboration

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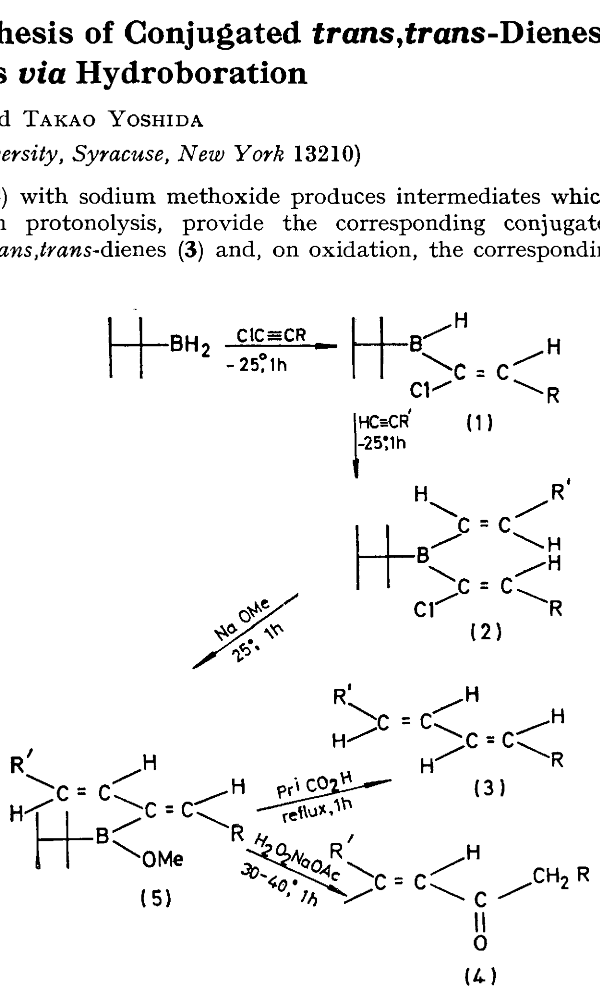
Summary A highly stereoselective (98—99%) and general synthesis of conjugated *trans,trans*-dienes and *trans*-alkenyl ketones involving a novel class of organoborane [1-chloroalk-1-enyl-(1,1,2-trimethylpropyl)boranes (**1**)] is reported.

Despite recent developments in the stereoselective syntheses of olefins,[1] there are still many classes of olefin that cannot be accommodated in both stereoselective and general manners. We report here a highly stereoselective and general synthesis of conjugated *trans,trans*-dienes† and *trans*-alkenyl ketones, which involves the intermediacy of a novel class of organoborane (**1**) containing both an olefinic group and an active boron-hydrogen bond. The reaction of terminal alkynes, such as hex-1-yne, with an equimolar quantity of 1,1,2-trimethylpropylborane does not produce alk-1-enyl-(1,1,2-trimethylpropyl)boranes in high yields.‡ The difficulty appears to lie in the concomitant formation of dialkenyl-(1,1,2-trimethylpropyl)boranes as well as of the corresponding *gem*-dibora-derivatives. On the other hand, we have found that the corresponding reaction of 1-chloroalk-1-ynes with 1,1,2-trimethylpropylborane at −25° produces 1-chloroalk-1-enyl-(1,1,2-trimethylpropyl)boranes (**1**) in 70—80% yields, as evidenced by ^{1}H n.m.r. analysis of the methanolysis products. The vinyl and methoxy signals of 1-chlorohex-1-enyl(methoxy)-1,1,2-trimethylhexylborane appear at δ 5·72 (t, J 7 Hz) and 3·72 (s). The organoborane (**1**), containing both an olefinic group and a boron–hydrogen bond appears to be the first reported example of such species.

More importantly, (**1**) can hydroborate terminal alkynes to form totally 'mixed' organoboranes (**2**). Treatment of (**2**) with sodium methoxide produces intermediates which, on protonolysis, provide the corresponding conjugated *trans,trans*-dienes (**3**) and, on oxidation, the corresponding



Scheme

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† A few stereoselective methods for the syntheses of symmetrically substituted *trans,trans*-dienes have been reported.[2,3] The reduction of conjugated diynes with sodium in ammonia, a reagent system which selectively reduces isolated alkynes to *trans*-olefins,[4] fails to produce the corresponding *trans,trans*-dienes.[5]

‡ For example, the maximum yield of hex-1-enyl-(1,1,2-trimethylpropyl)borane observed by us is only 20%.[5]

Preparation of conjugated trans,trans-*dienes and* trans-*alkenyl ketones*[a]

1-Halogenoalk-1-yne ($RC\equiv CX$) R	X	Alk-1-yne ($R'C\equiv CH$) R′	*trans,trans*-Diene or *trans*-alkenyl ketone	Yield (%) G.l.c.	Yield (%) Isolated	Isomeric purity (%)
$\mathrm{Bu^n}$	Br	$\mathrm{Bu^n}$	Dodeca-5,7-diene[b]	56		99
$\mathrm{Bu^n}$	Cl	$\mathrm{Pr^n}$	Undeca-4,6-diene[c]	63	45[d]	99
$\mathrm{Bu^n}$	Br	$\mathrm{Pr^n}$	Undeca-4,6-diene	51		98
$\mathrm{Bu^n}$	I	$\mathrm{Pr^n}$	Undeca-4,6-diene	21		85
$\mathrm{Bu^n}$	Cl	Ch*	1-Cyclohexylocta-1,3-diene[e]	59	55[d]	98
Ch*	Cl	$\mathrm{Bu^n}$	1-Cyclohexylocta-1,3-diene	53		98
$\mathrm{Bu^n}$	Cl	$\mathrm{Pr^n}$	Undec-4-en-6-one[f]	58	48	99
$\mathrm{Bu^n}$	Cl	Ch*	1-Cyclohexyloct-1-en-3-one[g]	54	48	99

[a] All new products gave correct elemental analyses and satisfactory spectral data. [b] n_D^{26} 1·4615 (lit.,[2] n_D^{25} 1·4635). [c] B.p. 46—48°, at 1 mmHg; n_D^{26} 1·4618. [d] The reaction mixture was oxidized with 3N-sodium hydroxide and 30% hydrogen peroxide after protonolysis. [e] B.p. 112—115° at 3 mmHg; n_D^{26} 1·4905. [f] B.p. 59—62° at 0·4 mmHg; n_D^{25} 1·4486. [g] B.p. 91—92° at 0·2 mmHg; n_D^{26} 1·4777. * Ch = cyclohexyl.

conjugated *trans*-alkenyl ketones (**4**).§ On these bases, the structure (**5**) may be assigned to the intermediates. The present diene synthesis is applicable to the preparation of both symmetrically and unsymmetrically substituted dienes. G.l.c. examination (SE-30) revealed that, except for a minor amount (*ca.* 5%) of the side product arising from the migration of 1,1,2-trimethylpropyl group and a few other unidentified peaks with considerably longer retention times, the desired product in each case appeared as an essentially single peak in the expected region. The *trans* geometry of the products was indicated by the i.r.[985s cm^{-1}] and ^1H n.m.r. spectra. In the case of dodeca-5,7-diene, the essential absence ($<1\%$) of the *cis,trans*- and *cis,cis*-isomers was further established by g.l.c. (co-injection with authentic samples of these isomers).[7] The experimental procedures are outlined in the Scheme. Tetrahydrofuran was used as the solvent except in the protonolysis step. Although the formation of dienes does not require oxidation, it is recommended that the mixture should be oxidised with alkaline hydrogen peroxide after protonolysis in order to avoid possible contamination of the dienes with boron-containing by-products during distillation. In the preparation of *trans*-alkenyl ketones, use of a stronger base, such as sodium hydroxide, in the oxidation causes isomerization of the products. The excess of sodium methoxide was neutralized with the stoicheiometric quantity of acetic acid prior to the oxidation.

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§ The reaction of 1-halogenoalk-1-ynes with dialkylboranes has provided stereoselective syntheses of *trans*-mono-olefins.[6]

[1] See, for example, D. J. Faulkner, *Synthesis*, 1971, 175.

[2] G. Zweifel and R. L. Miller, *J. Amer. Chem. Soc.*, 1970, **92**, 6678.

[3] M. F. Semmelhack, P. M. Helquist, and J. D. Gorzynski, *J. Amer. Chem. Soc.*, 1972, **94**, 9234.

[4] See, for example, H. O. House, 'Modern Synthetic Reactions', 2nd edn., Benjamin, Menlo Park, California, 1972, p. 205.

[5] E. Negishi and T. Yoshida, unpublished results.

[6] (*a*) G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *J. Amer. Chem. Soc.*, 1971, **93**, 6309 and references cited therein; (*b*) E. J. Corey and T. Ravindranathan, *ibid.*, 1972, **94**, 4013; (*c*) E. Negishi, J. J. Katz, and H. C. Brown, *Synthesis*, 1972, 555.

[7] (*a*) G. Zweifel, N. L. Polston, and C. C. Whitney, *J. Amer. Chem. Soc.*, 1968, **90**, 6243; (*b*) G. Zweifel and N. L. Polston, *ibid.*, 1970, **92**, 4068.