Acknowledgments. The authors are grateful to Drs. C. Moser, P. Cremaschi, and R. Ladner for interesting discussions. W. J. H. wishes to thank the Centre des Recherches, Roussel Uclaf, for a generous fellowship.

* Address correspondence to Department of Chemistry, University of California, Irvine, Calif. 92664.

Fernando Bernardi
Centre Européen pour le Cacul Atomic et Moléculaire
Centre d'orsay, Orsay, France

Warren J. Hehre*
Laboratoire de Chimie Théorique, Université de Paris-Sud
Centre d'Orsay, Orsay, France

Received November 6, 1972

A Convenient and General Synthesis of Acetylenes *via* the Reaction of Iodine with Lithium 1-Alkynyltriorganoborates

Sir:

Treatment of lithium 1-alkynyltriorganoborates with iodine under mild conditions produces the corresponding alkyne in essentially quantitative yields (eq 1–3).

$$\mathrm{HC{\equiv}CR} + n\text{-}\mathrm{BuLi} \longrightarrow \mathrm{LiC{\equiv}CR} + n\text{-}\mathrm{BuH} \quad (1)$$

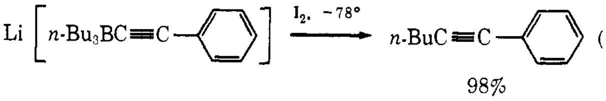
$$\mathrm{R'_3B} + \mathrm{LiC{\equiv}CR} \longrightarrow \mathrm{Li[R'_3BC{\equiv}CR]} \quad (2)$$

$$\mathrm{Li[R'_3BC{\equiv}CR]} + \mathrm{I_2} \longrightarrow \mathrm{R'C{\equiv}CR} + \mathrm{R_2BI} + \mathrm{LiI} \quad (3)$$

The reaction is applicable to a wide variety of alkyl and aryl acetylenes and organoboranes. Consequently, unlike conventional methods for the preparation of acetylenes based on nucleophilic substitution reactions of the alkali metal acetylides, the present procedure readily permits the introduction of both primary and secondary alkyl groups and can even be extended to the introduction of aryl groups. This procedure, with its exceptionally broad range of applicability, provides a new simple, general synthesis of acetylenes.

Trialkylboranes, readily prepared *via* hydroboration,[1] react with alkali metal acetylides to produce the corresponding alkali metal 1-alkynyltrialkylborates (eq 2).[2] Such compounds react with a variety of electrophiles, such as acids and acid halides, to induce transfer of an alkyl group from boron to carbon.[2c,d,3] Treatment of similar complexes of vinylorganoboranes with iodine results in an alkyl migration from boron to carbon, followed by a spontaneous deiodoboronation of the intermediate, to provide a highly convenient synthesis of olefins.[4] We undertook to explore the possibility of utilizing the reaction of iodine with alkali metal 1-alkynyltriorganoborates as a possible route to the corresponding alkynes.

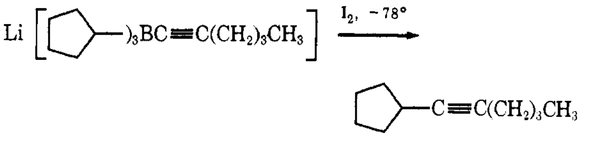
Addition of a solution of iodine in tetrahydrofuran (THF) to a solution of the complex from tri-*n*-butylborane and phenylethyne in THF at 0° resulted in the immediate disappearance of the iodine color. After stirring the reaction mixture for 0.5 hr, glpc analysis revealed a 67% yield of 1-phenyl-1-hexyne. At −78° the reaction of the iodine was much slower. However, stirring for 1 hr, followed by gradual warming to room temperature, brought the reaction to completion. A 98% yield of the desired alkyne was produced (eq 4).



(4)

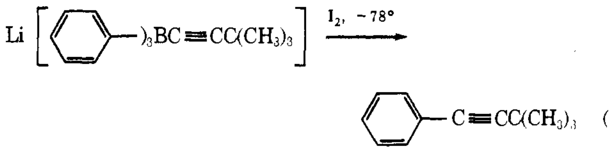
98%

There appears to be no difficulty in introducing secondary alkyl groups, such as *sec*-butyl, cyclopentyl, or cyclohexyl (eq 5). Finally, even aryl groups are readily introduced (eq 6).



(5)

100%



(6)

94%

The results of representative reactions are summarized in Table I.

Table I. The Synthesis of Acetylenes *via* the Reaction of Iodine with Lithium 1-Alkynyltriorganoborates

Acetylene[a]	Organoborane,[a] R_3B, R =	Product	Yield,[b] %
1-Hexyne	*n*-Butyl	5-Decyne	96
	Isobutyl	2-Methyl-4-nonyne	98
	sec-Butyl	3-Methyl-4-nonyne	98
	Cyclopentyl	1-Cyclopentyl-1-hexyne	100
	Cyclohexyl	1-Cyclohexyl-1-hexyne	99
	Phenyl	1-Phenyl-1-hexyne	98
Phenylethyne	*n*-Butyl	1-Phenyl-1-hexyne	98
	Isobutyl	1-Phenyl-4-methyl-1-pentyne	96
	sec-Butyl	1-Phenyl-3-methyl-1-pentyne	95
	Phenyl	Diphenylacetylene	95
3,3-Dimethyl-1-butyne	*n*-Butyl	2,2-Dimethyl-3-octyne	91
	Isobutyl	2,2,6-Trimethyl-3-heptyne	93
	Phenyl	1-Phenyl-3,3-dimethyl-1-butyne	94

[a] 10 mmol in 10 ml of THF. [b] By glpc based on acetylene.

The following procedure for the preparation of 1-phenyl-3,3-dimethyl-1-butyne is representative. A dry 500-ml flask equipped with a magnetic stirring bar, septum inlet, and dropping funnel was flushed with nitrogen. The flask was charged under nitrogen with 7.47 g (30.8 mmol) of triphenylborane and 25 ml of dry THF, then cooled to 0°. In another dry nitrogen-flushed flask equipped with a magnetic stirring bar and septum inlet was placed 50 ml of THF and 2.54 g (31 mmol) of 3,3-dimethyl-1-butyne. The flask was cooled in an ice bath and 16.4 ml (30.8 mmol) of a 1.88 *M* solution of *n*-butyllithium in hexane was added to form

---

(1) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972.

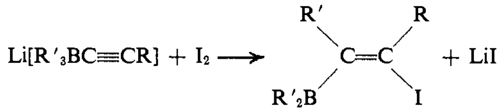
(2) (a) G. Wittig and P. Raff, *Justus Liebigs Ann. Chem.*, **573**, 195 (1951); (b) G. Wittig and D. Wittenberg, *ibid.*, **606**, 1 (1957); (c) P. Binger, G. Benedikt, G. W. Rotermund, and R. Köster, *ibid.*, **717**, 21 (1968); (d) P. Binger and R. Köster, *Tetrahedron Lett.*, 1901 (1965).

(3) M. Noruse, T. Tomita, K. Uchimoto, and H. Nozaki, Abstracts of the 27th Annual Meeting of the Chemical Society of Japan, Part I, 148 (1972).

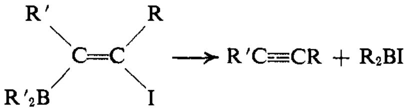
(4) G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 3652 (1967).

the acetylide. The lithium acetylide solution was then transferred into the 500-ml flask. The reaction solution was cooled to −78° and a solution of 7.87 g (31 mmol) of iodine in 75 ml of ethyl ether was added through the dropping funnel over a 0.5-hr period with efficient stirring. After an additional 45 min at −78°, the reaction mixture was allowed to warm to room temperature. The solution was then twice washed with 20 ml of 3 *N* sodium hydroxide (containing 1 ml of saturated sodium thiosulfate to remove residual iodine). The aqueous phase was extracted with 25 ml of ether. The combined organic phase was then treated with 32 ml of 3 *N* aqueous sodium hydroxide[5] followed by the dropwise addition of 10.5 ml of 30% hydrogen peroxide to oxidize the borinic acid by-product. Saturation of the aqueous phase with potassium carbonate yielded an organic phase in which glpc analysis revealed a 94% yield of product. The organic layer was separated, dried over potassium carbonate, and distilled. There was obtained 4.04 g (83%) of 1-phenyl-3,3-dimethyl-1-butyne, bp 100° (20 mm), n^{20}D 1.5175 (lit.[6] bp 84° (10 mm), n^{20}D 1.5230).

The reaction may be considered to be related to the Zweifel synthesis of cis olefins *via* the treatment of vinyldialkylboranes with iodine in the presence of alkali.[4] In the case of the vinyldialkylboranes, an iodonium species has been postulated as an intermediate in the transfer of an alkyl group from boron to carbon.[4] Such an intermediate is less probable for acetylenes, and we have no evidence requiring such a species in the present case. Electrophilic attack of iodine on the triple bond would presumably introduce a partial positive charge on the acetylenic carbon atom adjacent to the boron atom. Migration of the group from boron to the electron deficient carbon atom would produce the β-iodovinylborane (eq 7), postulated to be an intermediate. Such derivatives are known to undergo dehaloboration readily.[7] Such a dehaloboration would give the observed product (eq 8).



(7)



(8)

Probably the most general method previously available for the synthesis of acetylenes involves the reaction of alkali metal acetylides with organic halides or sulfates.[8] However, this synthesis is really satisfactory only for alkyl groups which readily undergo nucleophilic substitution reactions. The present synthesis is free of this limitation. Secondary and aryl groups appear to be introduced as easily as primary groups. Consequently, the present synthesis provides a range of applicability far broader than the procedures previously available.

---

[5] In the case of aromatic boranes, 3 mol of base per mol of borinic acid is used to neutralize the phenol and the boric acid. In the case of aliphatic boranes, only 1 mol of base per mol of intermediate is adequate for the oxidation.

[6] B. S. Kupin and A. A. Petrov, *Zh. Obshch. Khim.*, **31**, 2958 (1961).

[7] J. J. Eisch and L. J. Gonsior, *J. Organometal. Chem.*, **8**, 53 (1967).

[8] C. A. Buehler and D. E. Pearson, "Survey of Organic Synthesis," Wiley-Interscience, New York, N. Y., 1970.

[9] Graduate research assistant on Grant No. GM 10937 from the National Institutes of Health. Partial assistance provided by a cooperative research program under NSF Grant No. GP 27742X is also acknowledged.

Akira Suzuki, Norio Miyaura, Shigeo Abiko, Mitsuomi Itoh
Department of Chemical Process Engineering, Hokkaido University
Sapporo, Japan

Herbert C. Brown,* James A. Sinclair,[9] M. Mark Midland
Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received February 17, 1973

A Novel Ring Contraction of $O^{5'}$-6(*S*)-Cyclo-5-diazouridine. Elimination of a Ring Carbonyl Group in Preference to Diatomic Nitrogen

Sir:

We wish to report an unusual reaction observed in connection with our studies on the thermal stability of certain 5-diazouracils.[1] We have now established that $O^{5'}$-6(*S*)-cyclo-5-diazouridine[1] (I) undergoes a novel ring contraction which proceeds with the loss of a ring carbonyl group in preference to diatomic nitrogen.

A solution of I (1.30 g) in acetonitrile[2] (200 ml) was heated in a steel reaction vessel at 100° for 18 hr and the solution then allowed to stand at ambient temperature for 18 hr to afford a white solid (II). Initial data indicated that I had been converted to uridine *via* a simple nitrogen elimination, since there was observed an absence of any absorption bands in the 2150-cm^{-1} region of the ir spectrum and specific peaks [B + H (112), B + 2H (113), S (133), M − 30 (214)] in the low resolution mass spectra were identical with those reported for uridine.[3] However, the uv spectrum of II revealed the absence of any absorption in the 230–346-nm region instead of the absorption maximum at 261 nm which is observed for uridine. Elemental analyses (C, H, N) were obtained for II and found to be consistent with the empirical formula $C_8H_{12}N_4O_5$[4] which definitely eliminated the possibility that II was uridine and established that carbon monoxide had been lost in preference to diatomic nitrogen. The structure of II was established on the basis of the following data.

The pmr spectra (DMSO-d_6, DMSO-d_6–D_2O) of II revealed a pattern of peaks in the δ 3.5–6.5 region which were indicative of a ribofuranosyl moiety. The presence of D-ribose was subsequently confirmed by treatment of II with dilute acid followed by a direct paper chromatographic comparison of the hydrolysate with authentic D-ribose and D-arabinose. This facile hydrolysis suggested that the ribosyl moiety was still bonded to a ring nitrogen. The pmr spectra of II also revealed the presence of two broad, exchangeable singlets (δ 7.75 and 7.50) which were suggestive of an amide group. Corroboration for the presence of a carboxamido group was provided when II gave a posi-

---

[1] T. C. Thurber and L. B. Townsend, *J. Heterocycl. Chem.*, **9**, 629 (1972).

[2] Mallinckrodt Chemical Works, St. Louis, Mo., Nanograde.

[3] K. Biemann and J. A. McCloskey, *J. Amer. Chem. Soc.*, **84**, 2005 (1962).

[4] The yield of purified material corresponding to this empirical formula was 78%.