

Treatment of 1.00 mmole of triethylborane at 25° with 3.00 mmoles of silver nitrate or 1.50 mmoles of silver oxide in water (2.0 ml.) solution or suspension resulted in only a sluggish reaction, producing only minor amounts of *n*-butane, ethane and ethylene (decomposition products of ethylsilver¹) in 18–24 hours. Thus, in 18 hours the reaction involving silver oxide produced 9% *n*-butane, 5% ethylene and 15% ethane.

The addition of sodium hydroxide exerted a remarkable effect on the reaction. Thus the presence of 3.0 mmoles of sodium hydroxide in the silver oxide–triethylborane reaction mixture at either 25° or 0° brought about a very rapid reaction, complete in a matter of minutes.

These experiments with the volatile, inflammable triethylborane were carried out in an all-glass high vacuum apparatus. In a typical experiment, triethylborane, 1.00 mmole, was condensed on a mixture of 3.0 mmoles of sodium hydroxide and 1.51 mmole of silver oxide in 2.0 ml. of water. The vessel was warmed to 25° and the pressure observed. Within 10 minutes the pressure rose to 400 mm. and became sensibly constant. The volatile products were removed, measured, and analyzed on a silver nitrate–benzyl cyanide column. There was obtained 1.08 mmoles of *n*-butane (72%), 0.27 mmole of ethylene (9%), and 0.27 mmole of ethane (9%), accounting for 90% of the ethyl groups.

The reaction proceeds in methanol with similar results. In this solvent it was possible to attempt the reaction at lower temperatures. At –24° the decomposition of the intermediate ethylsilver is slow¹ and the hydrocarbon products appear at a significant rate only if the temperature is raised to 0° and above. No significant difference was observed in experiments in which silver oxide (or hydroxide) was formed *in situ* from silver nitrate and sodium hydroxide.

From these results, it is evident that in contrast to the behavior of tetraethyllead in its reaction with silver nitrate¹ all three ethyl groups of the triethylborane are utilized, $\text{Et}_3\text{B} + 3\text{AgOH} + \text{NaOH} \rightarrow 3\text{EtAg} + \text{NaB}(\text{OH})_4$. Consequently, this reaction provides a more economical means of utilizing alkyl groups and permits the preparation of ethylsilver in a medium free of another organometallic as by-product.

In the same way sodium hydroxide brings about a rapid reaction at 25° of triethylborane with auric oxide (formed *in situ* from auric chloride and sodium hydroxide) producing 74% *n*-butane, 16% ethylene and 1% ethane.⁴ The reaction with platinumic oxide (formed *in situ* from platinumic chloride) was more sluggish and differed also from the preceding reactions in not producing *n*-butane—the product was predominantly ethane: 57% ethane, 8% ethylene. Triethylborane is quite stable under these conditions in the absence of the platinumic oxide.

The decomposition of ethylsilver is believed to involve free radicals.¹ Treatment of silver oxide with sodium hydroxide and triethylborane in the presence of carbon tetrachloride resulted in a

(4) Dimethylodogold, $(\text{CH}_3)_2\text{AuI}$, is stable in ethyl alcohol at room temperature, but is decomposed in this solvent by alkali with the deposition of gold: F. H. Brain and C. S. Gibson, *J. Chem. Soc.*, 762 (1939).

marked decrease in yield of *n*-butane (12%), with the formation of a considerable amount of ethyl chloride (36%). Similarly, when the triethylborane–silver oxide–sodium hydroxide reaction was carried out in methanol containing styrene (1 *M*), the production of *n*-butane was markedly reduced (from 61% to 12%), and styrene largely disappeared from the solution.

These observations suggest that this reaction provides a new, simple route to ethylsilver and related derivatives, as well as a highly promising means of generating free radicals in aqueous and methanolic solutions. We are presently exploring the full scope of this new entry into free radical chemistry.

The financial assistance of the Ethyl Corporation in this study is gratefully acknowledged.

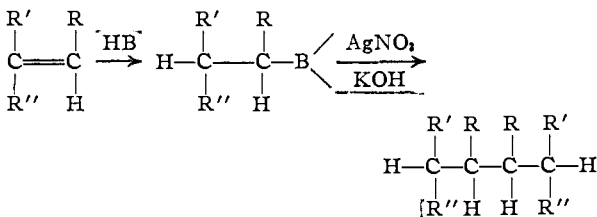
RICHARD B. WETHERILL LAB. HERBERT C. BROWN
PURDUE UNIVERSITY NORMAND C. HÉBERT
LAFAYETTE, INDIANA CARL H. SNYDER

RECEIVED JANUARY 10, 1961

THE REACTION OF TRIALKYLBORANES WITH ALKALINE SILVER NITRATE—A NEW GENERAL COUPLING REACTION

Sir:

We wish to report a new general coupling reaction which provides a highly convenient route for the conversion of olefinic derivatives into their saturated dimers. The synthesis involves the hydroboration of the olefinic derivative,¹ followed by the successive treatment *in situ* with solutions of sodium or potassium hydroxide and silver nitrate.²



The coupling reaction for simple terminal olefins, such as 1-butene, 1-hexene and 1-octene, is conveniently carried out with aqueous solutions of the reagents. In this way there was obtained from 1-hexene, coupled at –20°, a 79% yield of dodecane;³ at 0°, a 71% yield.

1-Hexene, 8.4 g., 0.100 mole, was hydroborated with sodium borohydride and boron trifluoride etherate in 57.5 cc. of diglyme. Water, 20 cc., was added to destroy residual hydride, then 120 cc. of 2.0 *M* aqueous potassium hydroxide. The mixture

(1) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4233 (1960).

(2) The reaction of Grignard reagents with silver bromide has been utilized for couplings: J. H. Gardner and P. Borgstrom, *ibid.*, **51**, 3375 (1929). It has also been reported that alkylboronic acids react with ammoniacal silver oxide (Tollens reagent) at elevated temperatures to yield coupled products: H. R. Snyder, J. A. Kuck and J. R. Johnson, *ibid.*, **60**, 105 (1938); J. R. Johnson, M. G. VanCampen, Jr., and O. Grummitt, *ibid.*, **60**, 111 (1938). In the present study ammoniacal silver oxide proved to be unsatisfactory for bringing about the coupling reaction with the trialkylboranes.

(3) The product was predominantly *n*-dodecane with approximately 6% of 5-methylundecane. The latter presumably arises from the 6% of the secondary boron derivative formed in the usual hydroboration of a terminal olefin: H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

