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, $Et_3B + 3AgOH + NaOH \rightarrow 3EtAg + NaB(OH)_4$. 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 byproduct.

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. The reaction with platinic oxide (formed in situ from platinic 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 platinic 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

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.

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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; 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

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).

⁽⁴⁾ Dimethyliodogold, (CH₄)₃Aul, 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

was cooled to 0° and 24.0 cc. of 5.0 M aqueous silver nitrate was added with stirring over ten minutes. After one hour at 0°, the product was extracted with pentane. Vapor phase chromatographic analysis indicated 66% n-dodecane, 5% 5-methylundecane and 20% of a mixture of 1-hexene and n-hexane.

The coupling reaction for more hindered olefins, such as 2-methyl-1-pentene and cyclohexene, gives better yields in methanol solution, presumably because of the greater difficulty of reaction of potassium hydroxide with the more hindered organoborane in the two phase aqueous system.

2-Methyl-1-pentene, $8.4~\rm g.$, $0.100~\rm mole$, was hydroborated as above. After destruction of residual hydride with 20 cc. of methanol, 120 cc. of 2.0 M potassium hydroxide in methanol was added. This was followed by 24.0 cc. of 5.0~M aqueous silver nitrate added over ten minutes with stirring, maintaining the temperature at 20–30°. After one hour, 100 ml. of water was added and the product isolated by extraction with pentane. Vapor phase chromatographic analysis indicated the presence of 71% of a single dodecane and 16% of a mixture of 2-methyl-1-pentene and 2-methylpentane. Distillation yielded $5.24~\rm g.$, (61%) of 4.7-dimethyldecane, b.p. 194-196° at $742~\rm mm.$, $n^{20}\rm D$ $1.4225.^4$

Yields of terminal olefins, as described above, are in the range of 60-80%. Internal olefins form the coupled products with yields in the range of 35-50%.

The reaction has been applied to a large number of olefins and appears to be quite general (product in parentheses): 1-butene (n-octane), 1-octene (n-hexadecane), isobutylene (2,5-dimethylhexane), 2-butene (3,4-dimethylhexane), cyclopentene (bicyclopentyl), cyclohexene (bicyclohexyl), 2-methyl-2-butene (2,3,4,5-tetramethylhexane)⁵ and anethole (dimethyl ether of hexestrol).

The hydroboration reaction can tolerate many different functional groups. Consequently, this coupling reaction should find very wide applicability in synthetic chemistry.

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

(4) I. N. Nazarov and G. P. Verkholetova, Zhur. Obshcheš Khim. (J. Gen. Chem.), 18, 1086 (1948), report b.p. 92.5-95° at 23 mm., n²⁰D 1.4230.

(5) Vapor phase chromatographic examination (Ucon Polar column) revealed the presence in nearly equal amounts of the two diastereoisomers (meso and racemic) to be anticipated for this structure. Resolution was not achieved for 4.7-dimethyldecane and 3,4-dimethylhexane in the vapor phase chromatographic analysis.

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RECEIVED JANUARY 10, 1961

A NOVEL SYNTHESIS OF CYCLOPROPENES

Sir:

We wish to report a reaction resulting in the formation of a cyclopropenyllithium compound conveniently convertible into cyclopropene derivatives which are otherwise difficult to prepare. When methylene chloride is added to a solution of 1,2-dimethylpropenyllithium (I) in tetrahydrofuran at -35° , the resulting solution contains

2,3,3-trimethylcyclopropenyllithium (VI) as evidenced by the transformations: hydrolysis of the reaction mixture yields 1,3,3-trimethylcyclopropene (V) (b.p. 45° (750 mm.); n^{20} D 1.3893; anal. found: C, 87.14; H, 12.43), carboxylation gives 2,3,3-trimethylcyclopropene-1-carboxylic acid (VII) (m.p. 48.5°; anal. found: C, 66.62; H, 8.04) and treatment with methyl iodide results in the formation of tetramethylcyclopropene (IX) (b.p. 67° (755 mm.); n^{20} D 1.4021; anal. found: C, 87.43; H. 12.32).

Structures of compounds V, VII and IX, which were obtained in 40 to 50% yield¹ are based on spectral and chemical evidence. Confirmation of the carbon skeleton was obtained by catalytic hydrogenation of V to 1,2,2-trimethylcyclopropane. The endocyclic position of the double bond follows from the n.m.r. spectrum of V, which exhibits narrowly spaced doublets at 9.08 (0.7 c.p.s. separation, relative intensity 6) and 8.10 τ (1.1 c.p.s. separation, relative intensity 3), and a multiple (relative-intensity 1) centered at 3.45 τ , the resonances of the gem. dimethyl, allylic methyl and olefinic protons, respectively. The infrared spectrum of the olefin is

in agreement with structure V (H—C=, 3070 cm. $^{-1}$; >C=C<, 1755 cm. $^{-1}$). The structure of carboxylic acid VII is also confirmed by the observed spectral data (n.m.r.: sharp lines at 8.88, (CH₂)₂C=CLiCH₁ + CH₂Cl₂ \longrightarrow

$$: CHCI + (CH_{4})_{2}C = CHCH_{4} + LiCI$$

$$CH_{4}$$

$$: CHCI + I$$

$$(CH_{3})_{2}C = C$$

$$CH_{4}$$

$$(CH_{3})_{2}C = C$$

$$CH_{5}$$

$$(CH_{4})_{2}C = C$$

$$CH_{5}$$

$$(CH_{4})_{2}C = C$$

$$CH_{6}$$

$$CH_{7}$$

$$CH_{7}$$

$$CH_{7}$$

$$CH_{8}$$

$$CH_{1}$$

$$CH_{1}$$

$$CH_{1}$$

$$CH_{2}$$

$$CH_{3}$$

$$CH_{4}$$

$$CH_{4}$$

$$CH_{5}$$

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$$CH_{4}$$

$$CH_{4}$$

$$CH_{5}$$

$$CH_{5}$$

$$CH_{5}$$

$$CH_{7}$$

7.82 and $-2.28~\tau$, relative intensities 6:3:1; infrared: >C=O, 1690 cm. $^{-1}$; >C=C< 1822 cm. $^{-1}$; ultraviolet: $\lambda_{\rm max}$ (hexane) 237 m μ , ϵ 7000). On treatment with diazomethane in ether at -15° VII is converted into its methyl ester (VIII) (b.p. 57° (15 mm.); n.m.r.: sharp lines at 8.98, 7.93 and 6.42 τ , relative intensities 2:1:1; infrared: >C=O, 1700 cm. $^{-1}$; >C=C< 1820 cm. $^{-1}$; ultraviolet: $\lambda_{\rm max}$ (hexane 226 m μ , ϵ 7700). Finally the tetramethyl-cyclopropene (IX) shows the anticipated spectral properties (n.m.r. sharp lines of equal intensities at

(1) Yields are based on three moles of I.