reaction temperature rose to over 200° in less than 20 minutes and a 68% yield of the beta-adduct was isolated.

The use of the copper(I) chloride, the diamine, and the monoamine thus exerts a very powerful catalytic effect on silicon hydride-olefin addition reactions. Inasmuch as the two amines and the acrylonitrile (or other olefin) can each form complexes with copper(I) chloride and possibly with the chlorosilane, it is presently difficult to speculate about a mechanism for this addition reaction. The catalyst system presumably functions as a strong base to polarize the silicon–hydrogen bond, thereby facilitating a beta-addition of the silicon to the acrylonitrile. It is also possible that an amine–copper(I)–acrylonitrile complex is formed rendering the olefin double bond more susceptible to nucleophilic attack. Additional experiments pertaining to this catalyst system and addition reaction will be reported later.

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THE REACTION OF MIXED TRIALKYLBORANES WITH ALKALINE SILVER NITRATE—HYDROBORATION AS A CONVENIENT ROUTE FOR THE SYNTHESIS OF CARBON STRUCTURES

Sir:

The very ready coupling of hydroborated olefins in situ by silver nitrate in the presence of alkali[1] prompted a study of the reaction of mixed organoboranes with the reagent. The results demonstrate that this new approach to the formation of carbon-to-carbon bonds should possess general applicability for the synthesis of hydrocarbon structures.

Equimolar mixtures of 1-hexene with 1-pentene, 2-methyl-1-butene, cyclopentene and 2-methyl-2-butene were hydroborated and treated in methanolic solution with silver nitrate and potassium hydroxide as described previously.[1] In the case of 1-pentene and 2-methyl-1-butene, the yields of the three possible products were almost statistical: $C-10/C-11/C-12 = 1.0/2.0/1.0$. In the case of the olefins yielding secondary organoboranes, the yields of the C-11 products drop below those predicted on a statistical basis (Table I).

TABLE I

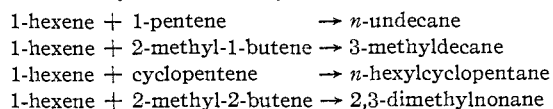EFFECT OF STRUCTURE ON MIXED COUPLINGS WITH 1-HEXENE

Olefin	Ratio 1-hexene/ olefin	Yield,[a] %	Products C-10	C-11	C-12
1-Pentene	1/1	66	1.00	2.00	1.00
2-Methyl-1-butene	1/1	64	0.97	1.88	1.00
Cyclopentene	1/1	54	0.44	1.05	1.00
2-Methyl-2-butene	1/1	52	0.45	1.02	1.00
1-Pentene	3/1	63	1.00	6.00	9.00
2-Methyl-1-butene	3/1	62	1.02	5.35	9.00
Cyclopentene	3/1	58	0.65	4.00	9.00
2-Methyl-2-butene	3/1	59	0.66	3.20	9.00

[a] Combined yield of C-10, C-11 and C-12 products based on the vapor phase chromatographic analysis.

(1) H. C. Borwn and C. H Snyder, J. Am. Chem. Soc., 83, 1002 (1961).

In a reaction involving a statistical coupling of two different alkyl groups, R and R', the maximum yield of the desired product can only be 50% of the coupled material, R_2, R–R', R'_2. However, there is the possibility of utilizing a large excess of a relatively cheap olefin to achieve a more nearly complete conversion of a second, more expensive olefin into the desired product. The practicality of this approach is indicated in Table I where a three-fold excess of 1-hexene over the C-5 olefin has given much higher conversions of the latter into the desired products.

The power of this new synthetic procedure is indicated by the above syntheses:

1-hexene + 1-pentene　　　　　→ n-undecane
1-hexene + 2-methyl-1-butene → 3-methyldecane
1-hexene + cyclopentene　　　 → n-hexylcyclopentane
1-hexene + 2-methyl-2-butene → 2,3-dimethylnonane

One limitation is evident. The two olefins should preferably differ in molecular weights so that the mixed product, RR', can be separated readily from the symmetrically coupled products, RR and R'R'. Fortunately, this is not a serious limitation since it is usually possible to select reactants to facilitate this separation.[2]

The hydroboration reaction can tolerate many functional groups (e.g., carbethoxy, nitro, sulfone) which cannot be present in Grignard reactions. Consequently, it is evident that this synthetic procedure for achieving desired carbon structures should prove a valuable adjunct to the Grignard synthesis.

(2) For example, the synthesis of 2-, 3-, and 4-methylnonane can be carried out with the appropriate butenes and hexenes, all commercially available.

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THE REACTION OF TRIETHYLBORANE WITH OXIDES OF SILVER, GOLD AND PLATINUM—A NEW CONVENIENT ROUTE TO NOBLE METAL ALKYLS AND TO FREE RADICAL CHEMISTRY

Sir:

In recent years the low temperature reaction of silver nitrate with lead alkyls, $R_4Pb + AgNO_3 \rightarrow RAg + R_3PbNO_3$, has been utilized as a convenient route to the unstable silver alkyls and related organometallics.[1] In the course of our program on the chemistry of trialkylboranes, we were led to explore the possible utility of triethylborane for the synthesis of ethylsilver and related noble metal alkyls.[2] The interesting chemical possibilities of these unstable derivatives have long been evident.[3]

(1) C. E. H. Bawn and R. Johnson, J. Chem. Soc., 3923 (1960); C. E. H. Bawn and F. J. Whitby, ibid., 3926 (1960).

(2) The reaction of mercuric oxide and lead (II) oxide with triethylborane at 70–80° has been utilized recently for the synthesis of stable organometallics, such as diethylmercury and tetraethyllead: J. B. Honeycutt, Jr., and J. M. Riddle, J. Am. Chem. Soc., 82, 3051 (1960).

(3) J. H. Gardner and P. Borgstrom, ibid., 51, 3375 (1929).