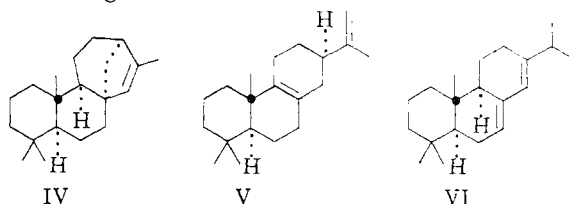


Further support for rimuene's C-13 configuration (III_d) came from an inspection of the optical rotatory dispersion curves of rimuene and the three resin acids (III_a,_b,_c), while isopimaric (III_a) and sandaracopimaric (III_b) acids have plain negative curves, pimaric acid (III_c) and rimuene have plain positive curves.^{3d,e} Since C-13, the asymmetric center surrounded by both chromophores in all four compounds, would be expected to be the major contributor to the sign and shape of these curves, the o.r.d. data confirm a pimaric-type C-13 stereochemistry for rimuene.

The consequent formulation III_d for rimuene precludes the latter's reported acid-catalyzed conversion^{2b} to isophyllocladene (IV)⁹ by a mechanism analogous to the suggested¹ and recently proved¹⁰ path of biosynthesis of tetracarbocyclic diterpenes. Instead, nuclear double bond and 13-methyl migrations could be expected to lead to a mixture of abietadienes from which both isophyllocladene (IV) (via diene V) and the reported^{2b} second product VI can emerge.¹¹



NOTE ADDED IN PROOF.—Through the courtesy of Professor Petri the m.m.p. of his and Edwards' samples of sandaracopimaric acid was measured and their infrared and n.m.r. spectra compared. The former was undepressed and the latter identical.

(9) Cf. P. K. Grant and R. Hodges, *Tetrahedron*, **8**, 261 (1960); R. F. Church, R. E. Ireland and J. A. Marshall, *Tetrahedron Letters*, No. **17**, 1 (1960); R. B. Turner and P. E. Shaw, *ibid.*, No. **18**, 24 (1960).

(10) A. J. Birch, R. W. Richards, H. Smith, A. Harris and W. B. Whalley, *Tetrahedron*, **7**, 241 (1959).

(11) Only the generous aid by Professor L. H. Briggs and by Dr. P. K. Grant (Wellington, New Zealand) in furnishing samples of rimuene, by Dr. O. E. Edwards (Ottawa, Canada) and Dr. R. V. Lawrence (Oluette, Florida) in supplying samples of sandaracopimaric acid and the other resin acids, respectively, and by Dr. W. A. Struck (Upjohn) in carrying out the o.r.d. measurements made our work possible.

(12) Public Health Service Predoctoral Research Fellow, 1960-1961.

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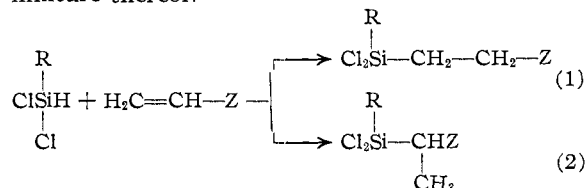
ERNEST WENKERT
PETER BEAR^{1,2}

RECEIVED DECEMBER 27, 1960

SILICON HYDRIDE-OLEFIN ADDITIONS

Sir:

We wish to report a new catalyst system which is unique in its effect on the addition of silicon hydrides to olefins containing double bonds conjugated with strongly electronegative groups. This addition reaction has been reported to occur, using a variety of catalysts, to give either an *alpha*- or a *beta*-adduct (reaction (2) or (1), respectively) or a mixture thereof.



The course of the reaction is determined by the nature of the electronegative group, Z, the presence of organic substituents on the olefinic carbon atoms, the type of group, R, attached to the silicon atom, and the kind of catalyst.

An unusual example of this reaction exists when Z is a nitrile group, *i.e.*, with acrylonitrile, and when R is a methyl group, as in methylchlorosilane, in that the *beta* addition (reaction 1) is effected poorly, if at all. Many catalysts for this reaction have been investigated, including tertiary amines,^{1,2,3} platinum-on-carbon,^{4,5} and amides.⁶ The best reported results² are those obtained with a pyridine catalyst in acetonitrile solvent at 160-170°, whereupon less than a 10% yield of *beta*-cyanoethylmethylchlorosilane was isolated. Using a platinum catalyst⁴ a 26% yield of the *alpha*-adduct was obtained after 26 hr. at 75°. In contrast, trichlorosilane adds to acrylonitrile^{7,8,9} to give relatively good yields of either *alpha*- or *beta*-cyanoethyltrichlorosilane.

The catalyst system which we have found facilitates the preparation of *beta*-cyanoethylmethylchlorosilane in yields greater than 75%. Three components are involved in this catalyst: tri-*n*-butylamine, N,N,N',N'-tetramethylethylenediamine, and copper(I) chloride. Low yields of *beta*-adduct result if the tributylamine is omitted and larger amounts of the diamine are substituted.

In a typical synthesis, a mixture of 23 ml. (0.22 mole) of methylchlorosilane, 10 ml. (0.15 mole) of acrylonitrile, 1.0 ml. (0.007 mole) of N,N,N',N'-tetramethylethylenediamine, 4.0 ml. (0.017 mole) of tri-*n*-butylamine, and 2.0 g. (0.02 mole) of copper (I) chloride was heated under reflux for 40 hours. During this time the temperature of the refluxing reaction mixture rose from 51° to over 126°. The darkly colored liquid was vacuum distilled to give 20 g. (79% of theoretical) of product, b.p. 83-85° (8 mm.) (lit.² for *beta*-cyanoethylmethylchlorosilane, b.p. 111-113° (40 mm.)). Infrared analysis is consistent with the structure of the *beta*-adduct and indicates the absence of the *alpha*-adduct (lit.⁴ b.p. 60-62° (4 mm.)).

As an indication of the scope of this three-component catalyst we have examined the reaction of other silicon hydrides and other olefins and find the present catalyst beneficial for the synthesis of many other *beta*-adducts. Of immediate interest is the addition of trichlorosilane to acrylonitrile reported¹ to give a 56% yield of *beta*-cyanoethyltrichlorosilane after 24 hr. reflux using 5 mole % of tri-*n*-butylamine as a catalyst. When an equimolar amount of trichlorosilane was used in place of methylchlorosilane, in the experiment described above using the three catalyst components, the

(1) M. Prober, French Patent 1,118,500 (1956).

(2) A. D. Petrov and V. M. Vdovin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1490 (1957).

(3) K. Shiina and M. Kumada, "Memoirs of the Faculty of Engineering, Osaka City University," Japan, Vol. 1, Dec. 1959.

(4) L. Goodman, R. M. Silverstein and A. Benitez, *J. Am. Chem. Soc.*, **79**, 3073 (1957).

(5) F. P. MacKay, Ph.D. Thesis, Pennsylvania State University, June, 1956.

(6) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 427 (1959).

(7) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan.*, **29**, 322, 326 (1956).

(8) L. H. Sommer, F. P. MacKay, O. W. Steward and P. G. Campbell, *J. Am. Chem. Soc.*, **79**, 2764 (1957).

(9) R. A. Pike, J. E. McMahon, V. B. Jex, W. T. Black and D. L. Bailey, *J. Org. Chem.*, **24**, 1939 (1959).

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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RECEIVED JANUARY 5, 1961

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 alkali¹ 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

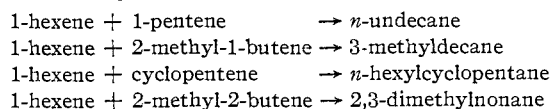
Olefin	Ratio 1- hexene/ olefin	Yield, ^a %	Products		
			C-10	C-11	C-12
1-Pentene	1/1	66	1.00	2.00	1.00
2-Methyl-1-butene	1/1	64	0.97	1.88	1.00
Cyclopentene	1/1	54	0.44	1.05	1.00
2-Methyl-2-butene	1/1	52	0.45	1.02	1.00
1-Pentene	3/1	63	1.00	6.00	9.00
2-Methyl-1-butene	3/1	62	1.02	5.35	9.00
Cyclopentene	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. Brown 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, R₂, 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:



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.

This investigation was made possible by Contract DA-33-008-ORD-2002 supported by the Office of Ordnance Research, U. S. Army, and by funds provided by the Ethyl Corporation. This assistance is gratefully acknowledged.

(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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RECEIVED JANUARY 10, 1961

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

Sir:

In recent years the low temperature reaction of silver nitrate with lead alkyls, R₄Pb + AgNO₃ → RAg + R₃PbNO₃, 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).