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# 3,322,807
# 1,4-BIS- AND 2,4-BIS-DI-(TRIORGANOSILYL) BUT-1-ENES

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The present invention relates to the dimerization of ω-olefinic silanes and is particularly directed to the process of dimerizing allyl and vinyl hydrocarbon silanes over trialkylaluminum or aluminum hydride catalysts. The invention is further directed to 1,4-bis(trihydrocarbylsilyl) but-1-enes and 2,4-bis(trihydrocarbylsilylmethyl)but-1-enes, which are produced in the dimerization process. The invention is further directed to tris(trihydrocarbylsilylethyl)aluminum, which is an intermediate as well as a product in the dimerization of the vinyl hydrocarbon silanes and to di(trihydrocarbylsilylethyl) 1,4-bis(trihydrocarbylsilyl)butyl-aluminum which is an additional intermediate.

It has been known heretofore that various olefinic hydrocarbons are capable of dimerization or other polymerization depended upon the particular olefinic hydrocarbon and catalyst employed. It has now been found that a controlled dimerization of allyl and vinyl hydrocarbon silanes can be effected with trialkylaluminum or aluminum hydride catalysts, and that the resulting dimers retain α-olefinic unsaturation.

The catalysts used in the present invention can be represented by the formula:

$$AlR_3$$

in which each R is a straight chain, branched, or cyclic saturated hydrocarbyl radical of up to 20 or more carbon atoms, or hydrogen. It is preferred that at least one R be an alkyl group, and more preferable for all three R's to be alkyl groups, including cycloalkyl groups, particularly those of up to 10 or so carbon atoms, e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, hexyl, cyclohexyl, octyl, decyl, etc., although other alkyls can be employed, e.g., dodecyl, eicosyl, etc.; in practice, alkyl aluminums containing no more than 6 carbon atoms in the alkyl group will generally be employed. Other suitable aluminum catalysts are, for example, cyclohexyldiethylaluminum, diethylaluminum hydride, isobutylaluminum dihydride, aluminum hydride, and triphenylethylaluminum.

In general, it will be preferable to employ alkyl aluminum compounds in which the alkyl group is branched on the β-carbon atom, e.g., such alkyl groups are isobutyl, 2-methylbutyl, 2-ethylbutyl, etc.; such branched alkyl groups are less prone to take part in the dimerization reaction that the normal alkyl groups, thereby avoiding any substantial co-dimerization reactions and improving the yield and purity of the desired dimer.

The allyl, vinyl, and other ω-olefinic hydrocarbon silanes employed in the present invention can be represented:

$$CH_2{=}CH{-}(CH_2)_n{-}\underset{\displaystyle R'}{\overset{\displaystyle R'}{\overset{|}{\underset{|}{Si}}}}{-}R'$$

in which $n$ is an integer from zero to 8 or more preferably zero or 1, and each R' is a hydrocarbyl radical of up to 10 or more carbon atoms, and ordinarily contains no non-benzenoid unsaturation, and can be the same as or different from each other R' in the molecule; each R' can, for example, be methyl, ethyl, phenyl, o-tolyl, p-tolyl, propyl, isopropyl, butyl, t-butyl, hexyl, cyclohexyl, decyl, etc. It is preferred that R' be an alkyl radical of up to 6 carbon atoms, or phenyl.



The dimerization of the allyl hydrocarbon silanes can be represented:

$$2R'_3SiCH_2CH{=}CH_2 \xrightarrow{AlR_3} R'_3SiCH_2CH_2CH_2\overset{\displaystyle CH_2}{\overset{\|}{C}}CH_2SiR'_3$$

in which R and R' are defined as having the meanings set forth hereinabove.

The 2,4-bis(trihydrocarbylsilylmethyl)but-1-ene products of the present invention include all such compounds having hydrocarbyl groups corresponding to those described hereinabove with respect to the allyl hydrocarbon silane reactants, particular reference being made to the definition of R' hereinabove. The products in this group of most practical value will probably be 2,4-bis(triphenylsilylmethyl)but-1-ene and 2,4-bis(trialkylsilylmethyl)but-1-enes in which the alkyl group has from 1 to 6 carbon atoms; 2,4-bis(trimethylsilylmethyl)but-1-ene, for example, is conveniently prepared.

The 2,4-bis(trihydrocarbylsilylmethyl)but-1-ene products have α-olefinic unsaturation and are capable of polymerization by free radical or Ziegler catalysts, either homopolymerization or copolymerization with vinyl or other monomers, e.g., ethylene, vinyl chloride, etc.; the but-1-ene products can also be hydrogenated or otherwise reduced to form the corresponding butanes; the unsaturation also provides a position for possible incorporation of hydroxyl, carboxyl, or other functional groups. The but-1-ene products may also be useful as functional fluids for transferring heat or mechanical energy, particularly in high temperature applications, or as additives for mineral oil or other lubricants to improve viscosity. The ω-olefinic hydrocarbon silanes, in which the olefinic group is further removed from the silicon than in the allyl silanes, will dimerize in the same manner and give products homologous to those obtained with the allyl silanes.

The dimerization of vinyl hydrocarbon silanes occurs in a different manner than the allyl silanes, and gives products which are non-analogous to those obtainable by reaction of olefinic hydrocarbons with trialkylaluminums. The reaction is represented:

$$3R'_3SiCH{=}CH_2 + AlR_3 \longrightarrow (R'_3SiCH_2CH_2)_3Al + 3 \text{ molecules olefin (formed from R)}$$

$$R'_3SiCH{=}CH_2 + (R'_3SiCH_2CH_2)_3Al \longrightarrow (R'_3SiCH_2CH_2)_2Al{-}\underset{\displaystyle SiR'_3}{\overset{|}{\underset{|}{CH}}}(CH_2)_3SiR'_3$$

$$R'_3SiCH{=}CH_2 + (R'_3SiCH_2CH_2)_2Al{-}\underset{\displaystyle SiR'_3}{\overset{|}{\underset{|}{CH}}}(CH_2)_3SiR'_3 \longrightarrow R'_3SiCH{=}CH{-}CH_2CH_2SiR'_3 + (R'_3SiCH_2CH_2)_3Al$$

in which R and R' have meanings as set forth hereinabove. When trialkylaluminums are employed in the above process, the formation of the tris(trialkylsilylethyl)aluminum compound in the first step is indicated by liberation of an alkylene, e.g., isobutylene when triisobutylaluminum is employed, and is confirmed by ethanol quenching of the reaction mixture of the two components, an ethyltrihydrocarbylsilane being the product, for example, ethyltriphenylsilane when vinyltriphenylsilane is the original reactant.

The 1,4-bis(trihydrocarbylsilyl)but-1-enes of the present invention include all such compounds having hydrocarbyl groups corresponding to those described hereinabove with respect to the vinyl hydrocarbon silane reactants, particular reference being made to the definition of R' hereinabove. The products in this group of most practical value will probably be 1,4-bis(triphenylsilyl)but-1-ene and 1,4-bis(trialkylsilyl)but-1-enes in which the alkyl group has from 1 to 6 carbon atoms; 1,4-bis(trimethylsilyl)but-1-ene, for example, is conveniently prepared. Similarly, the hydrocarbyl groups in the tris(trihydro-

carbylsilylethyl)aluminum can be any of the foregoing hydrocarbyl groups as generically or specifically described, the phenyl, ethyl, and methyl groups being of particular interest, and the hydrocarbyl groups of the bis(trihydrocarbylsilylethyl) - 1,4-bis(trihydrocarbylsilylbutyl)aluminum intermediates can likewise be any of the foregoing generically or specifically disclosed hydrocarbyl groups, especially phenyl, methyl and ethyl groups. The 1,4-bis (trihydrocarbylsilyl)but-1-enes of the present invention have olefinic unsaturation and are capable of polymerization by free radical or Ziegler catalysis, either homopolymerization or copolymerization with vinyl or other monomers, e.g., ethylene, vinyl cholride, etc.; the unsaturation in the but-1-ene products can also be used to introduce functional groups such as hydroxyl groups, carboxyl groups and the like, or can be hydrogenated or otherwise reduced to form the corresponding butanes. The but-1-ene products may also be useful as functional fluids for transferring heat or mechanical energy, possibly being particularly useful in high temperature and low temperature applications, or as additives for mineral oil or other lubricants to improve viscosity, or in general in any applications in which the properties of a medium molecular weight, internally unsaturated silicon-containing hydrocarbon are desirable.

The catalyst or metal co-reactant employed in the present invention consists essentially of trialkylaluminum or aluminum hydride catalysts and the process is carried out in the absence or substantial absence of other metals or metal compounds such as metal halides, particularly of transition metal halides, such as, for example, titanium tetrachloride. The presence of titanium tetrachloride, or other metal compound suitable for forming a Ziegler ethylene polymerization catalyst with aluminum alkyls or hydrides, causes the allyl silanes to polymerize to solids rather than to dimerize, and causes the vinyl silanes to give an uncertain mixture of products, depending upon conditions. In the present process, a good yield of dimer is obtained.

The following illustrate certain embodiments of the present invention. In the example, triisobutylaluminum is utilized as an exemplification of the alkyl aluminums and aluminum hydrides suitable for use in the present invention.

*Example 1*

A mixture of trimethylvinylsilane (50 g.) and triisobutylaluminum (2 g.) was heated in a sealed reactor at 200° C. for 12 hours. The cooled reaction mixture was diluted with about an equal volume of anhydrous ether and then shaken out with a 25 ml. portion of 10% $H_2SO_4$ followed by 2–20 ml. portions of water. The ether solution was dried over anhydrous magnesium sulfate and the solvent removed by distillation. The dimer, 1,4-bis(trimethylsilyl)but-1-ene, B.P. 81–83° C. (17 mm.), was obtained 64% yield; $n_D^{25}$ 1.4354. Analysis calculated for $C_{10}H_{24}Si_2$: C, 59.90; H, 12.07; Si, 28.02. Found: C, 59.97; H, 12.08; Si, 27.52.

*Example 2*

A mixture of triethylvinylsilane (25 g.) and triisobutylaluminum (1 g.) was heated at reflux. Initially, the pot temperature at reflux was 145° C., but gradually increased so that after 60 hours heating, no reflux was noted when the pot was maintained at 200° C. The reaction mixture was treated according to the procedure of Example 1 to isolate 1,4-bis(triethylsilyl)but-1-ene. The dimer, B.P. 171–173° C. (15 mm.); $n_D^{25}$ 1.4653, was obtained in 56% yield. Analysis calculated for $C_{16}H_{32}Si_2$: C, 67.57; H, 12.76; Si, 19.76; molecular weight 284.6. Found: C, 67.70; H, 12.92; Si, 19.58; molecular weight (freezing point in benzene), 285.

*Example 3*

A mixture of triphenylvinylsilane (28.6 g., 0.1 mole) and triisobutylaluminum (1 g., 0.005 mole) was heated at 195° C. As the silane melted, foaming and gas evolution was noted which would be indicative of an olefin exchange reaction. After heating at 195° C. for 24 hours, the reaction mixture solidified at reaction temperature. The reaction mixture was quenched by a short heating period with 50 ml. of ethanol at reflux and allowed to cool. The crystalline solid was separated by filtration and recrystallized from benzene. There was obtained 18 g. (64% yield) of colorless, crystalline product, M.P. 240° C. Analysis calculated for $C_{40}H_{36}Si_2$: C, 83.88; H, 6.33; Si, 9.82. Found: C, 83.86; H, 6.37; Si, 10.09.

The identity of the 1,4-bis(triphenylsilyl)but-1-ene products was confirmed by reducing the double bond therein by hydroalumination, followed by cleavage of the carbon-aluminum bond with alcohol to give 1,4-bis(triphenylsilyl)butane. Specifically, the tubane product was obtained by heating at reflux a mixture of 1,4-bis(triphenylsilyl)but-1-ene (3.5 g., 6 mmoles) in 50 ml. of o-xylene with triisobutylaluminum (2 g., 8 mmoles) to cause gas evolution and continuing the heating for a few minutes after gas evolution ceased. The cooled reaction mixture was then treated with 2 ml. of isobutano, causing a crystalline solid to separate, which was then recrystallized from benzene, to give 2.2 g. 1,4 - bis(triphenylsilyl)butane, M.P. 215–216° C. The mixed melting point with a sample of 1,4-bis(triphenylsilyl)butane prepared by reaction of 1,4-dichlorobutane and triphenylsilyllithium was also 215–216° C. The infra red spectra of the two samples were identical. To further confirm the course of the reaction of the vinyl silanes and trialkylaluminums as going in the indicated manner through tris(trihydrocarbylsilylethyl)aluminum, followed by reaction with additional vinyl silane to give di(trihydrocarbylsilylethyl) - 1,4 - (trihydrocarbylsilylbutyl)aluminum as a further intermediate, a reaction mixture of vinyltriphenylsilane and triisobutylaluminum which had been heated to 140° C. was quenched with ethanol to give ethyltriphenylsilane, thus clearly establishing the presence of tris(triphenylsilylethyl)aluminum, which would then react with additional vinyl silane to give the product according to the reaction scheme set forth above.

*Example 4*

A mixture of trimethylallylsilane (95 g.) and triisobutylaluminum (5 g.) was heated in a sealed reactor at 200° C. for 27 hours. The mixture was distilled and 65 g. (68% yield) of dimer, B.P. 96–100° C. (14 mm.) was obtained. An analytical sample of the 2,4-bis(trimethylsilylmethyl)but-1-ene was redistilled; B.P. 109–110° C. (22 mm.); $n_D^{25}$ 1.4439. Analysis calculated for $C_{12}H_{28}Si_2$: C, 63.07; H, 12.35; molecular weight, 228.5. Found: C, 63.25; H, 12.25; molecular weight (freezing point in benzene), 228.

*Example 5*

Allyltriphenylsilane (57 g.) and triisobutylaluminum (2 g.) were heated together at 200° C. Initially, a short period of effervescence of liberated isobutylene was noted. After heating for 24 hours, the cooled mixture was taken up in the minimum amount of ether. Chilling the ether solution in Dry Ice furnished 27 g. of crude dimer, M.P. 99–101° C. Recrystallizations from ethanol furnished 20 g. (36% yield) of dimer, M.P. 108° C. Analysis calculated for $C_{42}H_{40}Si_2$: C, 83.93; H, 6.71; Si. 9.35. Found: C, 84.03; H, 6.80; Si, 9.11.

The process of the present invention, whether using the allyl, vinyl or other $\omega$-olefinic silanes, is generally conducted in the absence of air, oxygen or other reactive gases, and often in an atmosphere of nitrogen or similar gas to insure inert atmosphere, with exclusion of moisture or other materials which would react with the aluminum compound reactants, as will be understood by those skilled in the art. The pressure at which the process is conducted is not important, sub-atmospheric, atmospheric, or superatmospheric conditions being suitable; often the process

is conducted in a sealed container under autogenous pressure to avoid loss of reactant material and to exclude air. The process is carried out at elevated temperatures varying from those relatively low temperatures just giving an appreciable dimerization reaction rate up to temperatures at which there is substantial decomposition of the aluminum compound reactants. Generally, the dimerization is effected above 100° C., particularly at temperatures of about 150° C. to about 225° C. In some cases, the first phase of the reaction to produce tris(trihydrocarbylsilylethyl)aluminum in the reaction of the vinyl silanes is readily effected at temperatures below 150° C. The proportions of the ω-olefinic silane reactants and the aluminum compound reactants can vary widely, as it is only necessary to have the aluminum compound present in catalytic amounts, but much larger amounts can be employed. In general, in order to avoid directing the reaction toward preparation of tris(trihydrocarbosilylethyl)aluminum to nearly substantial exclusion of the dimerization, it is desirable to have the aluminum compound constitute less than one-third of the silane reactant on a molar basis. Suitable ranges are, for example, 0.01 to 0.2 mole of the aluminum compound per mole of silane reactant, or often 0.05 to 0.1 mole of aluminum compound per mole of silane reactant. When the process is conducted in a continuous manner, a small amount of the aluminum compound can be added at the start and the silane reactant can then be added continuously or intermittently as consume. The aluminum alkyl can be recycled provided it has not been contacted with moisture, air, etc.

The reaction mixture can be treated in various manners as illustrated herein as convenient to separate the particular products produced. Often the products will be simply distilled, precipitated or extracted from the reaction mixture. In other cases it may be convenient prior to separation of the dimer product to destroy the concomitant tris-



(trihydrocarbylsilylethyl)aluminum compound by hydrolysis, alcoholysis or the like.

While the present disclosure sets forth certain proposals of the course of the dimerization of allyl and vinyl silanes, and provides substantiating data to support such proposals, it will be realized that the invention covers the dimerization reactions of the allyl and vinyl hydrocarbon silanes as claimed, regardless of the mechanism or course of the dimerization reaction.

What is claimed is:

1. As a compound, 1,4-bis(triphenylsilyl)but-1-ene.
2. As a compound, 1,4-bis(triethylsilyl)but-1-ene.
3. As a compound, 1,4-bis(trimethylsilyl)but-1-ene.
4. As a compound, 2,4-bis(triphenylsilylmethyl)but-1-ene.
5. As a compound, 2,4-bis(trimethylsilylmethyl)but-1-ene.


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