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The Stereochemistry of the Addition of Silicochloroform to Acetylenes. A Comparison of Catalyst Systems

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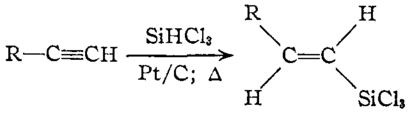
The stereochemistry of the addition of trichlorosilane to five substituted acetylenes has been studied in the presence of three different catalyst systems—platinized charcoal, chloroplatinic acid and benzoyl peroxide. Both the platinized charcoal and the chloroplatinic acid gave amazingly similar results—stereoselective *cis* additions resulting in *trans* products. It is suggested that the chloroplatinic acid may be reduced to metallic platinum, thus providing a surface upon which *cis* additions can occur. With benzoyl peroxide, a stereoselective *trans* addition occurred in the case of four of the acetylenes. 3,3-Dimethyl-1-butyne (*t*-butylacetylene) gave a mixture of *cis–trans* adducts in which the *trans* isomer predominated. In addition to this product, rather large amounts of diadduct were formed resulting from the addition of another molecule of trichlorosilane to *cis*-1-trichlorosilyl-3,3-dimethyl-1-butene. *trans*-1-Trichlorosilyl-3,3-dimethyl-1-butene would not react with trichlorosilane under similar conditions to form diadduct. *cis*-1-Trimethylsilyl-3,3-dimethyl-1-butene could be isomerized to the *trans* isomer with trichlorosilane and benzoyl peroxide, but no diadduct was formed in contrast to the behavior of the *cis*-trichlorosilyl compound. Implications of these findings are discussed.

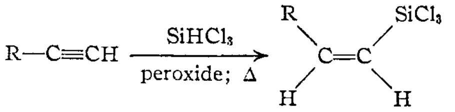
The addition of silanes ($\equiv$Si—H) to olefins and acetylenes has been studied extensively over a period of years.[1] Part of the interest in this reaction has stemmed from its commercial aspects[2] as well as the variety of conditions under which addition can be effected.

Recently we reported[3] that when trichlorosilane was added to various substituted acetylenes a stereoselective *cis* addition occurred when the reaction was catalyzed by platinized charcoal.



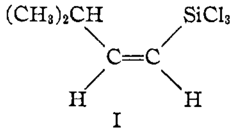
(*cis* addition; *trans* product) (1)

Likewise the peroxide-catalyzed addition of trichlorosilane to the same acetylenes was reported to give *trans* addition.[3]

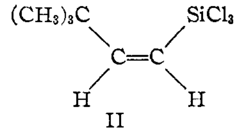


(*trans* addition; *cis* product) (2)

The present paper is an extension of the earlier work[3] to include a new catalyst system, chloroplatinic acid,[1g] as well as two new acetylenic substrates, 3-methyl-1-butyne (isopropylacetylene) and 3,3-dimethyl-1-butyne (*t*-butylacetylene). These two acetylenes were chosen for study because they provided a severe test for the generality proposed earlier[3] that benzoyl peroxide catalysis results in the *trans* addition of trichlorosilane with the formation of *cis* products. The *cis* adducts (I and II) formed in the case of these two acetylenes would be expected to be rather strained, particularly in the case of II, which, when methylated, is similar to *cis*-di-*t*-butylethylene.[4–6]



I



II

Since the advent of gas–liquid phase chromatography has greatly simplified the analysis of *cis–trans* mixtures of the type encountered in this study, we have re-analyzed some of the mixtures we obtained earlier by this technique and have included these results for the sake of completeness.

Benzoyl Peroxide Catalysis.—It will be noted from Table III that the addition of trichlorosilane to 1-pentyne, 1-hexyne, 1-heptyne and 3-methyl-1-butyne in the presence of benzoyl peroxide gave a mixture of *cis:trans* isomers which averaged about 3:1. Hence these additions are less stereoselective[7,8] than originally[3] was thought. Of particular significance was the result with 3,3-dimethyl-1-butyne, wherein, under the usual conditions of 20 hr. reaction time (Table III, entry 12), the *trans* adduct was obtained almost entirely. This has been the one exception noted thus far to the

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[1] (a) E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 484 (1948); (b) A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, *ibid.*, **69**, 2916 (1947); (c) C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2687 (1947); (d) C. L. Agre and W. Hilling, *ibid.*, **74**, 3895 (1952); (e) D. G. White and E. G. Rochow, *ibid.*, **76**, 3897 (1954); (f) J. L. Speier, R. Zimmerman and J. Webster, *ibid.*, **78**, 2278 (1956); (g) J. L. Speier, J. A. Webster and G. H. Barnes, *ibid.*, **79**, 974 (1957); (h) A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov and G. V. Odabashyan, *Izvest. Akad. Nauk S.S.S.R.*, **10**, 1206 (1957); (i) J. C. Saam and J. L. Speier, *J. Am. Chem. Soc.*, **80**, 4104 (1958); (j) J. W. Ryan, G. K. Menzie and J. L. Speier, *ibid.*, **82**, 3601 (1960).

[2] H. C. Miller and R. S. Schreiber, U. S. Patent 2,379,821 (1945); (b) A. J. Barry, D. E. Hook and L. DePree, U. S. Patent 2,626,268 (1953); (c) G. H. Wagner and C. O. Strother, U. S. Patent 2,632,013; (d) G. H. Wagner, U. S. Patent 2,637,738 (1953); (e) R. H. Krieble, U. S. Patent 2,524,529 (1950); (f) D. B. Hatcher, U. S. Patent, 2,532,493 (1950); 2,555,589 (1951); (g) Libbey-Owens-Ford Glass Co., British Patent 669,189 (1952).

[3] R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

[4] G. F. Hennion and T. F. Banigan, Jr., *ibid.*, **68**, 1202 (1946).

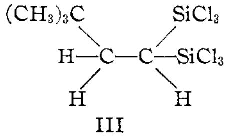
[5] F. L. Howard, T. W. Mears, A. Fookson and P. Pomerantz, *ibid.*, **68**, 2121 (1946).

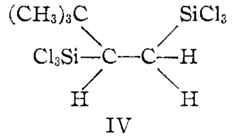
[6] W. H. Puterbaugh and M. S. Newman, *ibid.*, **81**, 1611 (1959).

[7] We have adopted the term "stereoselective" for our acetylene additions in accord with the definition of this term as set forth by H. Zimmerman, *et al.*, *ibid.*, **81**, 110 (1959). For an alternative usage, see F. G. Bordwell and P. S. Landis, *ibid.*, **80**, 6383 (1958).

[8] The earlier conclusion was based on the assumption that reductions of the substituted acetylenes catalyzed by Raney nickel produced almost exclusively *cis* olefin. The present results show this conclusion is not entirely valid, since V.P.C. analysis of 1-trimethylsilyl-1-hexene, prepared by the catalytic reduction of 1-trimethylsilyl-1-hexyne, gave a 3:1 *cis:trans* isomer mixture. Coincidentally, the benzoyl peroxide additions had produced mixtures with almost the same isomer ratio.

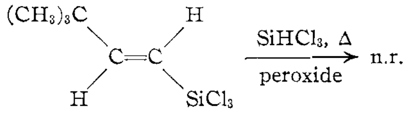
stereoselective *trans* addition of silicochloroform to acetylenes in the presence of peroxide catalysts. Of considerable interest was the isolation of a second product in this addition reaction. By elemental analysis this material was shown to be a diadduct, formed by the addition of another trichlorosilane molecule to the intermediate olefin. The exact structure of this material was not determined but, of necessity, it must correspond to III or IV below.


III


IV

It was demonstrated that this diadduct was not formed by the indiscriminate addition of the silicochloroform to *both* the *cis*- and *trans*-olefin. When an authentic sample of *trans*-1-trichlorosilyl-3,3-dimethyl-1-butene V was treated with trichlorosilane and peroxide, no reaction occurred. However, *cis*-1-trichlorosilyl-3,3-dimethyl-1-butene, treated under identical conditions, formed considerable amounts of the *trans* isomer along with the diadduct. Obviously compound II is strained relative to V and hence less activation energy is required to convert it to the diadduct.

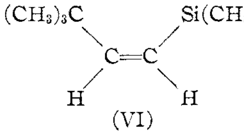
$$\text{II} \xrightarrow[\text{peroxide}]{\text{SiHCl}_3,\ \Delta} \text{III or IV} + \text{V} \qquad (3)$$


V (4)

$$(CH_3)_3C(H)C{=}C(H)SiCl_3 \xrightarrow[\text{peroxide}]{\text{SiHCl}_3,\ \Delta} \text{n.r.} \qquad (4)$$

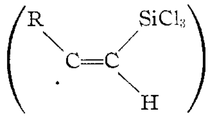
Further evidence for the strained nature of II was obtained when the preparation of an authentic sample of 1-trimethylsilyl-3,3-dimethyl-1-butene was attempted by the catalytic reduction of the corresponding acetylene. Even under very mild

$$(CH_3)_3CC{\equiv}CSi(CH_3)_3 \xrightarrow[\text{Ni, CH}_3\text{OH}]{H_2}$$

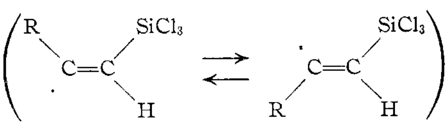

(VI) (5)

conditions (room temperature) the reaction proceeded slowly and resulted in rather considerable amounts of low boiling hydrogenolysis products. While these were not positively identified, they obviously resulted from an extremely facile cleavage of silicon–carbon bonds. Since the percentage of *cis* isomer obtained in this reduction was unusually low (44%), compared to the amount of *trans* compound obtained (20%), which is normal for these reductions, hydrogenolysis of the *cis* compound seemed to occur almost exclusively.

As might have been predicted, the yield of diadduct in reaction 3 was greatly diminished when the reaction between the trichlorosilane and 3,3-dimethyl-1-butyne was carried out with a 1:1 ratio of reactants rather than 2:1. In this instance some *cis* product was isolated (17%), although again the *trans* product predominated (83%). In still another run, samples were withdrawn periodically from the reaction mixture and analyzed (see Experimental, procedure C). Only a 10% variation in *cis:trans* isomer ratio was noted over a 15.5-hr. reaction time. Similar results were obtained in the addition of trichlorosilane to 1-heptyne initiated by benzoyl peroxide. In this case samples were withdrawn after 4, 10 and 20 hr. This *cis:trans* isomer ratio was essentially constant during this time. There are at least two possible explanations for these results. The addition of the trichlorosilyl radical to the acetylenes may occur with *complete* stereoselectivity yielding a radical, which, by reaction with trichlorosilane, will result in a *cis* product



However, before the termination step can take place, some isomerization of this radical might occur to one which would lead to *trans* product

[9]

Another explanation may be that the addition of trichlorosilane is simply indiscriminate, in that both *cis* and *trans* addition occurs, with the rate of the latter being approximately three times as great as the former. We are presently carrying out certain experimental tests which it is hoped will distinguish between these two possibilities. It is apparent that, except for *t*-butylacetylene, the peroxide-catalyzed addition of trichlorosilane tends to form principally the *cis* isomer through *trans* addition. In the case of the *t*-butylacetylene, however, the *cis* isomer is lost during the course of the reaction by isomerization to *trans* and by conversion to diadduct (eq. 3).

In order to test the stability of the *cis* isomers, various attempts were made to effect *cis–trans* isomerizations. A mixture of 79% *cis*- and 21% *trans*-1-trimethylsilyl-1-pentene was treated for varying lengths of time with (1) iodine and magnesium, (2) iodine and benzoyl peroxide, (3) methyl iodide and benzoyl peroxide. The iodine–benzoyl peroxide combination was found most effective in causing isomerization of the *cis* isomer. In a similar way, the isomerization of II and its trimethyl derivative VI was studied. Both compounds could be effectively isomerized to their respective *trans* isomers by refluxing them in cyclohexane with a mixture of trichlorosilane *and* benzoyl peroxide. Benzoyl peroxide or trichlorosilane *alone* caused only slight isomerization under similar conditions. These results would indicate

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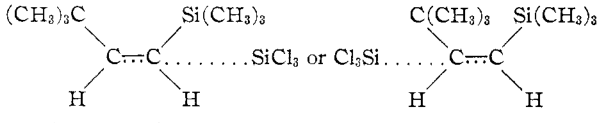
(9) There is little information available on this possibility. However it has been shown that certain stereoisomeric vinyllithium compounds do isomerize fairly rapidly at moderate temperatures. See Nesmeyanov and co-workers, *Tetrahedron*, **1**, 158 (1957); also D. Y. Curtin and co-workers, *J. Am. Chem. Soc.*, **77**, 4566 (1955). This can be taken as some evidence for the possibility of rearrangement of either vinyl carbanions or radicals. Some recent data on solvent effects (D. Y. Curtin and W. J. Koehl, *Chemistry & Industry*, 262 (1960), are interpreted in terms of carbanion isomerizations.

that the effective isomerizing agent was the iodine atom (generated by the reaction of benzoyl peroxide with iodine) or the trichlorosilyl radical (from trichlorosilane and benzoyl peroxide). Rather unexpectedly it was found that while *cis*-1-trimethylsilyl-3,3-dimethyl-1-butene (VI) was isomerized readily to *trans* by the benzoyl peroxide–trichlorosilane combination, no appreciable amount of the diadduct was formed at the same time. This was in sharp contrast to results with *cis*-1-trichlorosilyl-3,3-dimethyl-1-butene (II), where not only isomerization occurred, but also considerable amounts of the diadduct were formed (eq. 3). It is possible that, because of the bulk of the trimethylsilyl group (and the resulting strain in the molecule), the trichlorosilyl radical can weaken the olefinic bond sufficiently to cause isomerization by forming only a very weak bond with the olefinic carbon.[10]



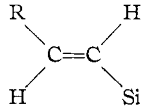
In the case of II, however, the trichlorosilyl radical might form a more complete bond[11] with the olefinic carbon. The more fully formed radical product can isomerize to *trans* product or react with trichlorosilane to form diadduct (III or IV). This postulate would lead to the interesting prediction that little or no silicon exchange should occur in the *cis* to *trans* isomerization of 1-trimethylsilyl-3,3-dimethyl-1-butene, while considerable silicon exchange should occur in the isomerization of II (eq. 3). We are presently checking this point.

Platinum–Charcoal and Chloroplatinic Acid Catalysis.—A re-examination of the platinum–charcoal-catalyzed additions of trichlorosilane to 1-pentyne, -hexyne and -heptyne, utilizing the more precise analytical method of vapor–liquid chromatography, disclosed exclusive *cis* addition (*trans* products resulting) as had been reported earlier.[3] Likewise, when the method was extended to include catalysis by chloroplatinic acid,[1g] almost exclusive *cis* addition was again found. In the case of the latter catalyst, the addition was also extended to the two new acetylenes, 3-methyl-1-butyne and 3,3-dimethyl-1-butyne. Again only *cis* addition was found.

In order to ascertain that the *trans* isomers in these reactions were not arising from isomerization of the less thermodynamically stable *cis*, a mixture of 21% *trans*- and 79% *cis*-1-trichlorosilyl-1-heptene was heated at 40–50° with catalytic amounts of chloroplatinic acid. At the end of four hours, the isomer ratio was essentially unchanged.

Since the active catalyst in the case of the chloroplatinic acid additions is the subject of some speculation,[12] two other experiments were run to demonstrate the stability of the *cis* isomers under the experimental conditions. In one case a mixture of 90% *cis*-1-trichlorosilyl-3,3-dimethyl-1-butene was refluxed for eight hours with trichlorosilane and chloroplatinic acid. Practically no change in the *cis:trans* isomer ratio occurred. In another experiment, a mixture of 81% *cis*-1-trichlorosilyl-1-hexene and 19% *trans* isomer was added to a reaction between 1-heptyne and trichlorosilane catalyzed by chloroplatinic acid. After eight hours, the 81:19 isomer ratio of the 1-trichlorosilyl-1-hexene was unchanged. Addition of the trichlorosilane to the 1-heptyne had proceeded normally. Clearly in the latter experiment, the active catalyst was present in the reaction mixture, and had not affected the *cis:trans* isomer ratio.

It was proposed earlier[3] that the *cis* additions in the case of the platinim–charcoal catalyst could be explained in a manner similar to the *cis* addition of hydrogen during catalytic hydrogenations. The silane is presumably adsorbed on the catalyst surface and adds to the acetylene *from one side only* (*cis* addition), resulting in a *trans*-olefin



The stereochemistry of the chloroplatinic acid additions are so remarkably similar that a surface reaction is again suggested. Another qualitative observation made during the chloroplatinic acid reactions suggests that this catalyst functions by a mechanism similar to that of the platinized charcoal. It was observed that an induction period occurs when chloroplatinic acid is used, during which time the small white silicone particles suspended in the solution (formed by the addition of an aqueous solution of the catalyst and the subsequent polymerization of some trichlorosilane) become coated with a black solid. It is this black solid which seems to be the active catalyst. It is quite possible that the chloroplatinic acid is reduced by the trichlorosilane to finely divided platinum which is adsorbed on the silicone particles. This idea is supported by the fact that platinized silica is known to be an effective catalyst for trichlorosilane additions.[2c] It must be borne in mind, however, that this proposal is purely a hypothesis at the present time which nicely explains the amazing similarity in stereochemistry between the platinized charcoal and the chloroplatinic acid catalyst systems. Further work is planned to test this hypothesis.

Experimental

Preparation of 1-Alkynes.—The 1-pentyne, 1-hexyne and 1-heptyne were prepared in essential accordance with the procedure of Jacobs.[13] The 3-methyl-1-butyne was made by the method of Boord,[14] and the 3,3-dimethyl-1-butyne was obtained by following the procedure of Puterbaugh and Newman.[6] The physical constants and yields obtained for these acetylenes are listed in Table I.

1-(Trimethylsilyl)-1-alkynes were prepared by a procedure already published (see ref. 3). Table II lists the physical properties, yields and analyses of these compounds.

Catalytic Reductions of Trimethylsilylalkynes.—The 1-trimethylsilylpentyne, -hexyne and -heptyne were reduced catalytically, using Raney nickel, in exactly the same fashion as described previously.[3] Analysis of the 1-trimethylsilyl-1-hexene thus prepared by vapor phase chromatog-

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[10] H. McConnell, *J. Chem. Phys.*, **20**, 1043 (1952).

[11] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[12] J. Saam and J. Speier, *ibid.*, **83**, 1351 (1961).

[13] "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 48.

[14] H. N. Miller, K. W. Greenlee, J. M. Derfer and C. E. Boord, *J. Org. Chem.*, **19**, 1882 (1954).

raphy[15] showed that it contained 75% *cis* and 25% *trans* isomer.

In a similar fashion, catalytic reduction of 1-trimethylsilyl-3-methyl-1-butyne gave a 79% yield of 1-trimethylsilyl-3-methyl-1-butene, boiling at 124–126°, $n^{20}\text{D}$ 1.4160. This material was shown to be a mixture containing 78% *cis* and 16% *trans* isomer, along with 6% starting material.

Catalytic reduction of 1-trimethylsilyl-3,3-dimethyl-1-butyne (0.1 mole, 15.4 g.) required 2–3 hours, contrasted to approximately 30 minutes for the other alkynes. Analysis showed the crude reduction product contained 16% of low boiling hydrogenolysis products, 44% *cis*- and 20% *trans*-olefin. In addition there was 13% unreacted starting material and 7% of an unknown, tentatively identified as 1-trimethylsilyl-3,3-dimethyl-1-butane. The pure *cis* isomer could be obtained from this mixture by careful fractionation through a Podbielniak column. It boiled at 149.5–150°, $n^{20}\text{D}$ 1.4328, and showed no band in the infrared[16] at 985 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{20}Si$: C, 69.14; H, 12.90. Found: C, 69.40; H, 13.00.

The peak for the *trans* isomer in this v.p.c. chromatogram was identical in retention time to that obtained for material prepared by adding trichlorosilane to 3,3-dimethyl-1-butyne using chloroplatinic acid as catalyst.

Benzoyl Peroxide-catalyzed Additions of Trichlorosilane.—For all of the alkynes except 3,3-dimethyl-1-butyne, the same procedure which was employed in the earlier work[3] was used. The 1-trichlorosilyl-1-alkenes were then methylated by refluxing them with methylmagnesium bromide or iodide as described earlier.[3] The products thus obtained are listed in Table III. The following procedures were used in the additions of trichlorosilane to 3,3-dimethyl-1-butyne.

(A) A mixture of 32.8 g. (0.4 mole) of 3,3-dimethyl-1-butyne, 108 g. (1.3 moles) of cyclohexane, 108 g. (0.8 mole) of trichlorosilane and 6.4 g. (0.026 mole) of benzoyl peroxide was refluxed for 20 hr. The product was distilled through a 50-cm. column packed with glass beads. A total of 34.3 g. (39%) of 1-trichlorosilyl-3,3-dimethyl-1-butene was obtained, boiling at 79–81° (35 mm.). Treatment of this product with methylmagnesium bromide afforded 18 g. (73%) of 1-trimethylsilyl-3,3-dimethyl-1-butene, boiling at 62–63° (60 mm.), $n^{20}\text{D}$ 1.4216. This material gave only one peak when subjected to vapor phase chromatography, and possessed a strong infrared band at 985 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{20}Si$: C, 69.14; H, 12.90. Found: C, 69.17; H, 12.74.

The pot-residue from the above reaction was also distilled, and a product (40.7 g.) boiling at 80–82° (1 mm.) was collected. Based on the formula $C_6H_{12}Si_2Cl_6$ this amounted to a 29% yield. After treatment with excess methylmagnesium bromide, followed by distillation, 21 g. (79%) of product boiling at 108–109° (23 mm.) was collected ($n^{20}\text{D}$ 1.4541). This material, adjudged to be a di-adduct, gave only one peak when subjected to v.p.c., and possessed an infrared spectrum with no olefin absorption peaks. Its n.m.r. spectrum had peaks at 6.85, 6.04, 5.49 and 5.42 p.p.m. relative to benzene. Their relative intensities were approximately 18:9:2:1.

Anal. Calcd. for $C_{12}H_{30}Si_2$: C, 62.51; H, 13.12. Found: C, 62.92; H, 13.14.

(B) The procedure listed in (A) above was repeated except that the ratio of the trichlorosilane to butyne was reduced to 1:1. A 68% yield of 1-trichlorosilyl-3,3-dimethyl-1-butene (b.p. 78–80° (35 mm.)) was obtained, along with a trace of di-adduct. After treatment with methylmagnesium bromide, the 1-trichlorosilyl-3,3-dimethyl-1-butene was shown by v.p.c. to contain 83% *trans* and 17% *cis* isomer.

(C) In this procedure the usual apparatus was modified by adding a glass tube extending to the bottom of the reaction flask and sealed with a piece of Tygon tubing and a pinch clamp. The ratio of trichlorosilane to butyne was reduced to 0.87. Samples (30 ml.) were removed at various times and added to an excess of methylmagnesium bromide. After hydrolysis, the solvents were removed under reduced pressure and vapor phase chromatograms were taken of the crude products. The results are

Time, hr.	*cis*, %	*trans*, %
2.5	34	66
6	33	67
18	24	76

1-Trimethylsilyl-3-methyl-1-butene.—Using the same procedure as described in (A) above, trichlorosilane was added to 3-methyl-1-butyne. The 1-trichlorosilyl-3-methyl-1-butene thus obtained (30.2 g., 37%) boiled at 56–57° (20 mm.). After alkylation with methylmagnesium bromide, 1-trimethylsilyl-3-methyl-1-butene (12.9 g., 61%) was obtained boiling at 122–124°, $n^{20}\text{D}$ 1.4179. This material consisted of 72% *cis* and 28% *trans* isomer.

Anal. Calcd. for $C_8H_{18}Si$: C, 67.52; H, 12.75. Found: C, 67.53; H, 12.75.

Table I

Physical Constants of 1-Alkynes

	B.p., °C.	$n^{20}\text{D}$	Yield, %
1-Pentyne[a]	40	1.3850	65
1-Hexyne[a]	71	1.3987	71
1-Heptyne[a]	99	1.4090	52
3-Methyl-1-butyne[b]	28	1.3725	59
3,3-Dimethyl-1-butyne[b]	39	1.3743	85

[a] A. Henne and K. Greenlee, *J. Am. Chem. Soc.*, **67**, 484 (1945). [b] See ref. 6.

Table II

1-Trimethylsilyl-1-alkynes

1-Trimethylsilyl-	B.p., °C.	$n^{20}\text{D}$	Yield, %
1-Pentyne[a]	135	1.4270	58
1-Hexyne[a]	155	1.4318	66
1-Heptyne[a]	176	1.4344	56
3-Methyl-1-butyne[b]	59 (73 mm.)	1.4203	60
3,3-Dimethyl-1-butyne[c]	57 (60 mm.)	1.4161	53

[a] See ref. 3. [b] *Anal.* Calcd. for $C_8H_{16}Si$: C, 68.48; H, 11.50. Found: C, 68.23; H, 11.65. [c] *Anal.* Calcd. for $C_9H_{18}Si$: C, 70.05; H, 11.76. Found: C, 70.20; H, 12.14.

Chloroplatinic Acid-catalyzed Additions of Trichlorosilane.—All of the chloroplatinic acid-catalyzed additions were carried out in a similar fashion. Typical directions are given below for the addition to 3-methyl-1-butyne and 3,3-dimethyl-1-butyne.

***trans*-1-Trimethylsilyl-3-methyl-1-butene.**—In a 200-ml. pressure bottle was placed 27 g. (0.2 mole) of trichlorosilane and 2 drops of 10% chloroplatinic acid. The mixture was shaken briefly until the evolution of HCl ceased, whereupon 6.8 g. (0.1 mole) of 3-methyl-1-butyne was added. The bottle was tightly stoppered and placed in an oil-bath maintained at 60–70°. After 3.5 hr. the bottle was removed, cooled in an ice-bath and opened. The contents were distilled to yield 16.1 g. (79%) of 1-trichlorosilyl-3-methyl-1-butene boiling at 60–61° (23 mm.).

From the reaction of 16.1 g. (0.079 mole) of 1-trichlorosilyl-3-methyl-1-butene and 0.5 mole of methylmagnesium bromide there was obtained 7.1 g. (63%) of *trans* 1-trimethylsilyl-3-methyl-1-butene, boiling at 124–125°, $n^{20}\text{D}$ 1.4180.

Anal. Calcd. for $C_8H_{18}Si$: C, 67.52; H, 12.75. Found: C, 67.23; H, 12.90.

***trans*-1-Trimethylsilyl-3,3-dimethyl-1-butene.**—A mixture of 27.0 g. (0.2 mole) of trichlorosilane, 8.2 g. (0.1 mole) of 3,3-dimethyl-1-butyne and 2 drops of 10% chloroplatinic acid was refluxed for 8 hours. Distillation of the product gave 10.9 g. (50%) of *trans*-1-trichlorosilyl-3,3-dimethyl-1-butene boiling at 67–69° (20 mm.).

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(15) An Aerograph model A-110-C and a Perkin-Elmer Vapor Fractometer model 154-C were used for all the analyses in this paper. A 5-ft. Ucon Polar column or a 2-meter polypropylene glycol column was found effective for all the separations except those involving derivatives of 3-methyl-1-butyne. In the latter instance, adiponitrile supported on 60–80 mesh firebrick was used.

(16) A peak in the 965–985 cm.$^{-1}$ region is considered of diagnostic value for a *trans* ethylene. See N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952); B. Loev and C. R. Dawson, *J. Am. Chem. Soc.*, **78**, 1180 (1956).

TABLE III

METHYLATED ADDUCTS ($RCH{=}CHSi(CH_3)_3$)

	Alkyne	Catalyst	Isomer distribution		Yield,[a] %	B.p.		$n^{20}D$
			cis, %	trans, %		°C.	Mm.	
1	1-Pentyne	Peroxide	79	21	77 (35)	64	60	1.4231
2	1-Pentyne	Pt/C		~100	65 (88)	135		1.4220
3	1-Pentyne	$H_2PtCl_6 \cdot 6H_2O$		~100	93 (84)	135		1.4225
4	1-Hexyne	Peroxide	77	23	78 (36)	60	20	1.4286
5	1-Hexyne	Pt/C		~100	82 (93)	60	20	1.4260
6	1-Hexyne	$H_2PtCl_6 \cdot 6H_2O$		~100	78 (74)	60	20	1.4260
7	1-Heptyne	Peroxide	75	25	74 (43)	100	69	1.4330
8	1-Heptyne	Pt/C		~100	48 (73)	100	69	1.4305
9	1-Heptyne	$H_2PtCl_6 \cdot 6H_2O$		~100	74 (77)	100	69	1.4301
10	3-Methyl-1-butyne	Peroxide	72	28	61 (37)	122–124		1.4179
11	3-Methyl-1-butyne	$H_2PtCl_6 \cdot 6H_2O$		~100	63 (79)	124–125		1.4180
12	3,3-Dimethyl-1-butyne	Peroxide		~100	73 (39)	62–63	60	1.4216
13	3,3-Dimethyl-1-butyne	$H_2PtCl_6 \cdot 6H_2O$		~100	64 (50)	62–63	60	1.4212

[a] The value in parenthesis is the yield (based on alkyne) of the addition of trichlorosilane to the substituted acetylene. The first value is the yield (based on trichlorosilyl adduct) of the Grignard alkylation.

1-Trichlorosilyl-3,3-dimethyl-1-butene (10.9 g., 0.05 mole) was added to 0.3 mole of methylmagnesium bromide in 200 ml. of ether. The mixture was hydrolyzed by an ammonium chloride solution; the ether layer dried over magnesium sulfate and then distilled. A total of 5 g. (64%) of *trans*-1-trimethylsilyl-3,3-dimethyl-1-butene boiling at 60–63° (60 mm.) ($n^{20}D$ 1.4212) was obtained.

Anal. Calcd. for $C_9H_{20}Si$: C, 69.14; H, 12.90. Found: C, 69.52; H, 13.14.

Isomerization of 1-Trimethylsilyl-1-pentene.—In separate reactions, 2.8 g. (0.02 mole) of 1-trimethylsilyl-1-pentene (79% *cis* and 21% *trans*) was refluxed with: (A) a mixture of 0.1 g. (0.004 mole) of iodine and 0.01 g. (0.004 g. atom) of 40 mesh magnesium; (B) a mixture of 0.1 g. (0.004 mole) of iodine and 0.05 g. (0.002 mole) of benzoyl peroxide; (C) a mixture of 2.8 g. (0.02 mole) of methyl iodide and 0.1 g. (0.004 mole) of benzoyl peroxide which was added in four portions, at the beginning of the reaction and again after 12, 24 and 36 hr. Samples were removed from the reaction flasks at various times and analyzed by v.p.c. The results are

Method	Time, hr.	cis, %	trans, %
A	3	76	24
A	10	71	29
B	3.5	64	36
B	9	59	41
C	48	77	23

Isomerization of *cis*-1-Trimethylsilyl-3,3-dimethyl-1-butene.—Pure *cis*-1-trimethylsilyl-3,3-dimethyl-1-butene (7.8 g., 0.05 mole), trichlorosilane (6.8 g., 0.05 mole), cyclohexane (13 g., 0.15 mole) and 0.8 g. of benzoyl peroxide were refluxed together for 20 hr. at 80°. The condenser was kept at −30° to keep the trichlorosilane from escaping. The reaction product was added to an excess of methylmagnesium bromide (0.2 mole). After stirring for 4 hours, the mixture was hydrolyzed, the solvents removed under reduced pressure and the crude product analyzed by v.p.c. An isomerization of 61% *cis*- and 39% *trans*-1-trimethylsilyl-3,3-dimethyl-1-butene had taken place, but no evidence of a di-adduct was found.

Under the same conditions, *trans*-1-trimethylsilyl-3,3-dimethyl-1-butene remained unchanged.

When *cis*-1-trimethylsilyl-3,3-dimethyl-1-butene (1.0 g., 0.0064 mole) was refluxed in cyclohexane (2.0 g., 0.024 mole) for 20 hr. with 0.1 g. of benzoyl peroxide only slight isomerization to a 92% *cis*–8% *trans* mixture occurred.

Isomerization of 1-Trichlorosilyl-3,3-dimethyl-1-butene.—A mixture of 10.9 g. (0.05 mole) of 88% *cis*–12% *trans*-1-trichlorosilyl-3,3-dimethyl-1-butene, 6.8 g. (0.05 mole) of trichlorosilane, 13.4 g. (0.15 mole) of cyclohexane and 0.8 g. of benzoyl peroxide was refluxed for 20 hr. The mixture was then added to an excess of methylmagnesium bromide (0.5 mole). After stirring for 6 hr. the mixture was hydrolyzed, the ether layer separated and dried, and the solvents removed under reduced pressure. The crude product contained 39% *trans*-olefin, 6% *cis* and 55% di-adduct.

Under the same conditions, *trans*-1-trichlorosilyl-3,3-dimethyl-1-butene remained unchanged.

When 2.2-g. (0.01 mole) samples of 88% *cis*–12% *trans*-1-trichlorosilyl-3,3-dimethyl-1-butene in 2.5 g. (0.03 mole) of cyclohexane were refluxed for 20 hr. with *either* 0.2 g. of benzoyl peroxide *or* 1.4 g. (0.01 mole) of trichlorosilane only a very small change in isomer distribution was noted.

Reaction of *cis*-1-Trichlorosilyl-3,3-dimethyl-1-butene with Trichlorosilane and Chloroplatinic Acid.—A mixture of 90% *cis*–10% *trans*-1-trichlorosilyl-3,3-dimethyl-1-butene (2.2 g., 0.01 mole), trichlorosilane (1.35 g., 0.01 mole) and 1 drop of 10% chloroplatinic acid was refluxed for 8 hr. The reaction mixture was then added to an excess of methylmagnesium bromide and stirred for 12 hours. The mixture was hydrolyzed with an ammonium chloride solution and the ether layer dried over magnesium sulfate. After the excess solvent was removed under reduced pressure, the crude product was analyzed by v.p.c. The isomer distribution had changed only slightly to 88.5% *cis* and 11.5% *trans*.

Chloroplatinic Acid-catalyzed Addition of Trichlorosilane to 1-Heptyne in the Presence of *cis*-1-Trichlorosilyl-1-hexene.—A mixture of 27.1 g. (0.2 mole) of trichlorosilane and 2 drops of 10% chloroplatinic acid was heated to reflux temperature, and a solution of 2.2 g. (0.01 mole) of 80.6% *cis*–19.4% *trans*-1-trichlorosilyl-1-hexene in 9.6 g. (0.1 mole) of 1-heptyne was added rapidly with stirring. After refluxing for 8 hours, the crude product was added to an excess of methylmagnesium bromide. The mixture was stirred for 18 hours and then hydrolyzed with an ammonium chloride solution. The ether layer was separated and dried over magnesium sulfate. After the ether was removed under reduced pressure, the crude product was analyzed by v.p.c. While the addition of trichlorosilane to 1-heptyne had proceeded readily, the isomer distribution of the 1-trichlorosilyl-1-hexene was unchanged.

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