[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

The Stereochemistry of the Addition of Silicochloroform to Acetylenes

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The stereochemistry of the addition of silicochloroform to three aliphatic 1-alkynes and phenylacetylene was investigated. The reactions were catalyzed either by benzoyl peroxide or platinized charcoal. Comparison of the infrared spectra of the adducts with those of authentic compounds showed that the peroxide-catalyzed reaction involves a stereospecific *trans* addition of the elements of H and $SiCl_3$ to produce *cis*-olefins, while platinized charcoal gives a stereospecific *cis* addition to produce *trans*-olefins. The stability of the products under the reaction conditions was demonstrated.

The addition of silicochloroform ($HSiCl_3$) to acetylenes and olefins is a well-known reaction[1] and the subject of several patents.[2]

The experimental conditions for the addition of $\equiv$SiH type compounds to unsaturated linkages have been varied. For example, peroxides[1a] and platinized charcoal[2d] have been used and even acid[3,4] and base.[5]

It seems likely that under certain of the aforementioned conditions (*e. g.*, peroxide-catalyzed) a free radical chain mechanism is operative.[6]

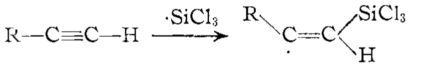
$$HSiCl_3 + \text{peroxide} \longrightarrow \cdot SiCl_3$$

$$\cdot SiCl_3 + {>}C{=}C{<} \longrightarrow \cdot \overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}SiCl_3$$

$$\cdot \overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}SiCl_3 + HSiCl_3 \longrightarrow H\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}SiCl_3 + \cdot SiCl_3$$

Since the stereochemistry of free radical addition reactions is of current interest,[7-12] it seemed appropriate to examine the stereochemistry involved in the addition of silicochloroform to acetylenes, particularly since some of these reactions are of considerable industrial interest.

The acetylenes chosen for study were 1-pentyne, 1-hexyne, 1-heptyne and phenylacetylene. If, indeed, the addition proceeds by the free radical chain shown above, the intermediate radical would have a rigid structure (see I below) in the case of acetylenes, and stereochemical trends should be detected easily.



$$R-C\equiv C-H \xrightarrow{\cdot SiCl_3} \overset{R}{\ } \diagdown C{=}C \diagup^{SiCl_3}_{\diagdown H} \qquad (I)$$

Excellent yields of adduct were obtained with all of the acetylenes when the platinum catalyst was employed. The peroxide catalyst gave moderate yields with the aliphatic alkynes. Peroxide-catalyzed additions to phenylacetylene were unsuccessful, with only starting material being recovered.

$$R-C\equiv CH + HSiCl_3 \xrightarrow[\text{or Pt/C}]{Bz_2O_2} RCH{=}CHSiCl_3$$

$$R = n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ n\text{-}C_5H_{11},\ C_6H_5\text{-}$$

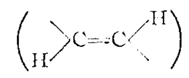
To ensure hydrolytic stability, the adducts obtained by either procedure were methylated with methylmagnesium halide or methyllithium. Simi-

$$RCH{=}CHSiCl_3 \xrightarrow[\text{or MeLi}]{MeMgX} RCH{=}CHSiMe_3$$

larly the adduct obtained from the platinum-catalyzed reaction with phenylacetylene was converted to the phenylated derivative by treatment with phenyllithium.

$$C_6H_5CH{=}CHSiCl_3 + C_6H_5Li \longrightarrow C_6H_5CH{=}CHSi(C_6H_5)_3$$

Infrared spectra of the peroxide-catalyzed adducts from 1-pentyne, 1-hexyne, 1-heptyne and phenylacetylene showed no strong peak in the 965–985 cm.$^{-1}$ region. A peak in this region is considered of diagnostic value[13,14] for a *trans*-ethylene



although it has been known to be misleading.[15,16]

To confirm the conclusion that *cis* products had resulted from these additions, authentic *cis* isomers were synthesized by an independent route. 1-Trimethylsilylpentyne, -hexyne, -heptyne and phenylethynyl-trimethylsilane were prepared by the sequence

$$R-C\equiv CH \xrightarrow[2,\ Me_3SiCl]{1,\ n\text{-}BuLi}$$

$$R-C\equiv CSiMe_3 \xrightarrow[\text{Raney Ni}]{H_2} cis\text{-}RCH{=}CHSiMe_3$$

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(1) (a) E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **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).

(2) (a) 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).

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(12) P. S. Skell, R. C. Woodworth and J. H. McNamara, *ibid.*, **79**, 1253 (1957).

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(15) C. F. Hiskey, H. L. Slates and N. L. Wendler, *J. Org. Chem.*, **21**, 429 (1956).

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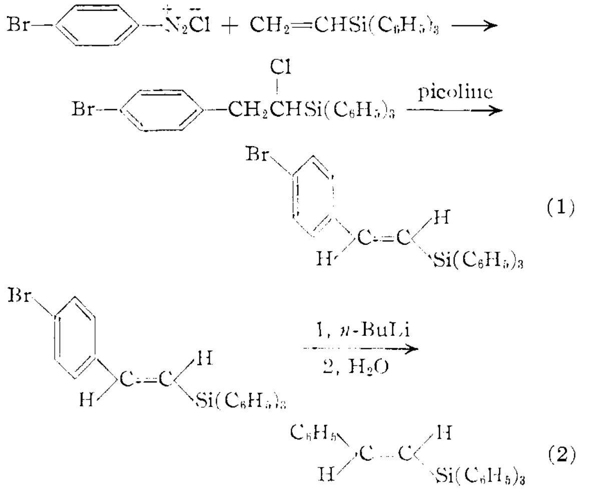
It has been shown that catalytic reduction of alkynes with Raney nickel and hydrogen gives predominantly the *cis*-olefin.[17] It was possible to carry out the reduction of the alkynylsilanes either in absolute ethanol or methanol; however, the latter solvent was found to be more convenient. While the alkynylsilanes were readily soluble in methanol, the *cis*-alkenylsilanes were insoluble in this solvent (except β-trimethylsilylstyrene). The products thus could be separated readily and used without further purification. Spectra of the peroxide-catalyzed adducts were almost identical with those of the authentic *cis* isomers, indicating essentially a stereospecific *trans* addition. Synthetic mixtures of *trans*-trimethylsilyl-1-hexene (prepared by the platinum reaction) and authentic *cis* isomer indicated that even a few per cent. of *trans* isomer when admixed with the *cis* could be detected readily by infrared.

The spectra of the adducts obtained from the platinum–charcoal-catalyzed additions showed a strong band at 985 cm.$^{-1}$ in contrast to the *cis* compounds. It was deemed desirable to synthesize an authentic *trans* isomer to verify that this band was indeed characteristic of the *trans* configuration. Accordingly the synthesis of *trans*-β-trimethylsilylstyrene was attempted from *trans*-β-lithiostyrene[18] and trimethylchlorosilane. This approach was unsatisfactory since the product was always badly contaminated with phenylethynyltrimethylsilane. An authentic *trans* isomer ultimately was synthesized successfully, however, by the route



Meerwein additions like that shown in reaction 1 were reported previously from this Laboratory.[19] Although the dehydrohalogenation of the Meerwein adduct can give a mixture of *cis–trans* isomers, the *cis* isomer would be formed to only a slight extent on the basis of steric considerations.[20] The purity of the *trans* isomer formed in this reaction was clearly indicated by its sharp melting point after only one recrystallization. This compound had a strong band[21] at 985 cm.$^{-1}$. The crude product, obtained by the reaction of phenyllithium with the platinum-catalyzed adduct of trichlorosilane to phenylacetylene, gave no mixed melting point depression with the authentic sample of *trans*-β-triphenylsilylstyrene. Furthermore their infrared spectra[21] were identical, thereby establishing the *trans* configuration of the platinum-catalyzed adduct.

It was necessary, of course, to ascertain whether isomerization had occurred during the addition reactions. This was accomplished by the following experiments. An authentic sample of *cis*-1-trimethylsilyl-1-hexene was heated in cyclohexane with benzoyl peroxide and trichlorosilane at 85° for 20 hours, stirred with trichlorosilane and platinized charcoal at 85° for five hours, and exposed to daylight for three days. A sample of *trans*-1-trimethylsilyl-1-hexene was heated at 85° with benzoyl peroxide, silicochloroform and cyclohexane for 20 hours. In none of these cases was any isomerization detected. Although these experiments were carried out with the methylated adducts it seems reasonable that the lability of the methylated and unmethylated adducts should be similar.

Although selective methylation conceivably could lead to the loss of one isomer, this does not appear to have happened. The adduct from either the platinum or peroxide-catalyzed addition could be methylated in yields up to 85% under comparable conditions indicating that selective methylation was essentially non-existent.

Discussion

The stereospecific *trans* addition noted in the presence of peroxide is in accord with the observations of Goering[7-10] and co-workers. The reason for the stereospecificity in this instance probably is the rigidity of the radical intermediate formed in the reaction (see Fig. 1). It has been found, for example, that certain other radical additions (wherein the radical intermediate is not rigid) are non-stereospecific.[11]

The stereochemistry of the platinum-catalyzed addition is of special interest. It has been suggested[22] that these additions are ionic in nature. Taken in conjunction with our results, this would strongly suggest that the –Si–H bond is polarized on the catalyst surface, such that the H becomes negative and the SI positive $(\overset{\overset{-}{\delta}}{\mathrm{H}}\cdots\overset{\overset{+}{\delta}}{\mathrm{Si}}\!\lessdot)$. This then adds to the olefin from *one side only* in a strictly *cis* fashion. In this regard the reaction closely resembles the commonly accepted picture for catalytic hydrogenation.

Experimental

***n*-1-Alkynes.**—The aliphatic acetylenes were prepared according to the procedure in reference 22a.

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(18) G. F. Wright, *J. Org. Chem.*, **1**, 457 (1937).

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(20) (a) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5855 (1952); (d) D. J. Cram, F. D. Greene and C. H. Depuy, *ibid.*, **78**, 790 (1956); (e) D. Y. Curtin, *Rec. Chem. Progr.*, **15**, 111 (1954).

(21) This was observed in a 0.026-mm. cell. The spectrum of the *cis* isomer was devoid of a band at 985 cm.$^{-1}$ when run as a capillary while the methylated platinum adduct showed a strong band. The *trans* isomer was run as a 0.200 *M* solution in carbon tetrachloride.

(22) L. Goodman, R. M. Silverstein and J. N. Shoolery, THIS JOURNAL, **78**, 4493 (1956).

(22a) "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 48.

	B.p., °C.	n^{20}D	Yield, %
1-Pentyne	40	1.3850[a]	65
1-Hexyne	71	1.3987[a]	71
1-Heptyne	99	1.4090[a]	51

[a] A. Henne and K. Greenlee, THIS JOURNAL, **67**, 484 (1945).

Phenylacetylene was prepared in 62% yield, n^{20}D 1.5494, according to the procedure of Hessler[23] or in a 67% yield, n^{20}D 1.5495, according to the procedure of Vaughn, *et al.*[24]

1-(Trimethylsilyl)-1-alkynes.—*n*-Butyllithium (1.0 mole) was prepared according to the procedure of Gilman and Jones.[25] The acetylene (1.0 mole) was added dropwise to the *n*-butyllithium cooled in an ice-bath. Stirring was continued for an additional 30 minutes. Trimethylchlorosilane (115 g., 1.0 mole) was added dropwise with cooling as required to moderate the reaction. The mixture was stirred for an additional 3 hours at room temperature. Hydrolysis was effected by pouring onto chipped ice. The ethereal solution was separated, washed, and dried. The product was fractionated through a Todd column.

	B.p., °C.	n^{20}D	Yield, %
1-Trimethylsilyl-1-pentyne[a]	135	1.4270[e]	24[d]
1-Trimethylsilyl-1-hexyne[b]	155	1.4318[e]	66
1-Trimethylsilyl-1-heptyne[c]	176	1.4344	56
Phenylethynyltrimethylsilane	67 (5 mm.)	1.5284[f]	64

[a] *Anal.* Calcd. for $C_8H_{16}Si$: C, 68.54; H, 11.50. Found: C, 68.30; H, 11.61. [b] *Anal.* Calcd. for $C_9H_{18}Si$: C, 70.10; H, 11.74. Found: C, 70.35; H, 11.74. [c] *Anal.* Calcd. for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 71.26; H, 11.97. [d] *m*-Propyllithium as the metalation agent gave a 58% yield. [e] K. Frisch and R. Young, THIS JOURNAL, **74**, 4853 (1952). [f] A. D. Petrov, L. L. Shchukoskaya and Y. P. Egorov, *Doklady Akad. Nauk, S.S.S.R.*, **93**, 293 (1953); *C. A.*, **48**, 13616*g* (1954).

Catalytic Reduction of Trimethylsilylalkynes.—A Parr hydrogenator was charged with 0.1 mole of the trimethylsilylalkyne, 50 ml. of absolute ethanol or methanol and 2 g. of Raney nickel. The theoretical amount of hydrogen was absorbed rapidly from an initial pressure of 4 atm.

	B.p. °C.	B.p. Mm.	n^{25}D
1-Trimethylsilyl-1-pentene	135		1.4222
1-Trimethylsilyl-1-hexene	60	20	1.4273
1-Trimethylsilyl-1-heptene	102	68	1.4310
β-Trimethylsilylstyrene	85	7	1.5096

Preparation of Platinum Catalyst.—The 10% platinum-on-charcoal catalyst was prepared according to the procedure of Vogel.[26]

Platinum-catalyzed Additions[27].—The alkyne (0.3 mole) was added over a 15-minute period to a rapidly stirred, refluxing suspension of 0.6 g. of 10% platinum-on-charcoal in 68 g. (0.6 mole) of trichlorosilane. The mixture was stirred at reflux for an additional 3 hours. The catalyst was removed by filtration and the product distilled through a Vigreux column.

	B.p. °C.	B.p. Mm.	Yield, %
1-Trichlorosilyl-1-pentene	77–79	35	86
1-Trichlorosilyl-1-hexene	79–80	16	93
1-Trichlorosilyl-1-heptene	104–106	25	73
β-Trichlorosilylstyrene	89–90	4	82

Peroxide-catalyzed Additions.—The alkyne (0.5 mole), 132 g. (1.5 moles) of cyclohexane (free from unsaturation), 134 g. (1.0 mole) of trichlorosilane and 8 g. (0.033 mole) of benzoyl peroxide were heated at 60–70° for 20 hours. The product was obtained by distillation at reduced pressure. Phenylacetylene gave no adduct under these conditions.

	B.p. °C.	B.p. Mm.	Yield, %
1-Trichlorosilyl-1-pentene	81–84	45	38
1-Trichlorosilyl-1-hexene	93–95	27	36
1-Trichlorosilyl-1-heptene	102–104	24	47

Methylation of Adducts.—The methylation of the trichlorosilylalkenes (0.2 mole) was carried out by refluxing them with methylmagnesium bromide or iodide (1.0 mole) in ether for 24 hours. After hydrolysis, the product was distilled to yield the trimethylsilylalkenes.

	B.p. °C.	B.p. Mm.	n^{20}D	Yield, %
1-Trimethylsilyl-1-pentene[a]	135		1.4220[d]	65
1-Trimethylsilyl-1-hexene[b]	60	20	1.4269[d]	82
1-Trimethylsilyl-1-heptene[c]	104	70	1.4310[d]	48
β-Trimethylsilylstyrene	81	5	1.5260[d]	68

[a] *Anal.* Calcd. for $C_8H_{18}Si$: C, 67.57; H, 12.78. Found: C, 67.38; H, 12.77. [b] *Anal.* Calcd. for $C_9H_{20}Si$: C, 69.12; H, 12.92. Found: C, 69.14; H, 13.21. [c] *Anal.* Calcd. for $C_{10}H_{22}Si$: C, 70.50; H, 13.02. Found: C, 70.51; H, 12.95. [d] The refractive indices for the *cis*- and *trans*-1-trimethylsilyl-1-alkenes agreed with each other by ±0.0010. However, note the profound difference between *cis*-β-trimethylsilylstyrene and the methylated platinum adduct (*trans*-configuration).

Phenylation of Platinum-catalyzed Adduct to Phenylacetylene.—Phenyllithium was prepared from 31.4 g. (0.2 mole) of bromobenzene in 50 ml. of ether and 2.8 g. (0.4 g. atom) of lithium wire in 50 ml. of ether. The adduct (11.9 g., 0.05 mole) was added dropwise. Stirring was continued for an additional three hours at room temperature. The reaction was hydrolyzed by pouring onto crushed ice. The ethereal solution was separated and dried. Evaporation of the solvent gave 14 g. (80%) of product which melted at 147–148.5° after washing with about 5 ml. of cold ethanol (lit.[28] m.p. 146–147°).

trans-β-**Triphenylsilylstyrene.**—Six grams (0.0125 mole) of the *p*-bromo Meerwein adduct[19] dissolved in 25 ml. of 4-picoline was heated at reflux for 24 hours. The picoline solution was dissolved in ether and washed free of the base with dilute hydrochloric acid. The solution was dried and the ether evaporated. The crude product was recrystallized once from ethanol–acetone.

The above material in 50 ml. of ether was added rapidly to 0.03 mole of *n*-butyllithium at 0°. Stirring was continued at 0° for 15 minutes. The reaction mixture was worked up in the usual manner. On evaporation of most of the ether white crystals separated. These were filtered and recrystallized from ethanol–acetone to give 1.1 g. (25%) of product, m.p. 148–148.5°.

trans-β-**Trimethylsilylstyrene.**—Two simultaneous preparations of β-styryllithium[18] from 1.05 g. (0.15 g. atom) of lithium wire in 20 ml. of ether and 9.15 g. (0.05 mole) of β-bromostyrene in 40 ml. of ether were added rapidly to a solution of 13.1 g. (0.12 mole) of trimethylchlorosilane in 20 ml. of ether. The mixture was heated at reflux for one hour and then worked up in the usual manner. Distillation of the product gave 3.4 g. (19%) of product boiling at 83–85° (6 mm.), n^{20}D 1.5300. The infrared spectrum (0.026-mm. cell) showed a strong *trans* band at 985 cm.$^{-1}$ and a moderate band at 2125 cm.$^{-1}$ characteristic of phenylethynyltrimethylsilane.

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(27) These directions were kindly supplied to us by Dr. Howard E. Rice of the General Electric Co., Waterford, N. Y.

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