includes λ_{max} 13.22 μ (lit. mp 97°,[4] $[\alpha]^{20}D$ −26°,[4] λ_{max} (in CS_2) 13.16 μ[11]).

Anal. Calcd for $C_{27}H_{45}Cl$: C, 80.05; H, 11.20; Cl, 8.75. Found: C, 80.24; H, 11.19; Cl, 8.45.

Reaction with Sodium Bromide.—To 50 ml of acetone were added 5.0 g (0.0110 mole) of cholesteryl chloroformate and 10.0 g (0.097 mole) of sodium bromide and the mixture was refluxed for 150 hr. Work-up as for cholesteryl chloride, but with only one recrystallization from acetone, gave 4.0 g of white crystals, mp 96–99°; infrared spectrum includes λ_{max} 13.23 and 14.22 μ (lit.[11] λ_{max} (in CS_2) at 14.21 μ for cholesteryl bromide).

Anal. Calcd for 59% $C_{27}H_{45}Br$ and 41% $C_{27}H_{45}Cl$: C, 75.52; H, 10.56; Br + Cl, 13.93. Found: C, 75.35; H, 10.60; Br + Cl, 13.96.

Cholesteryl Azidoformate.—To 50 ml of acetone were added 5.0 g (0.0110 mole) of cholesteryl chloroformate and 5.0 g (0.077 mole) of sodium azide and the mixture was refluxed for 24 hr. During reaction the λ_{max} for the carbonyl peak changed from 5.63 to 5.82 μ; longer reflux times, prior to evaporation to dryness of small samples for infrared spectrum determination, led to no significant decrease in the intensity of the 5.82 μ peak. Work-up as for cholesteryl chloride gave 4.7 g of crude cholesteryl azidoformate (93% yield), mp 92–95°.

A 3.00-g portion of the crude product was chromatographed on a column consisting of (by weight) four parts of Florisil[12] and one part of Celite.[13] The column was prepared using hexane and the azidoformate was eluted using a mixture of (by volume) three parts of benzene and seven parts of hexane. A 1.88-g fraction was found to be analytically pure cholesteryl azidoformate, mp 94.5–95.5°, $[\alpha]^{25}D$ −34.0°; infrared spectrum includes λ_{max} 4.59 (s), 4.63 (w), 4.70 (s),[14] 5.82 (s, C=O), and 8.15 (s and broad, CO)[15] μ.

Anal. Calcd for $C_{28}H_{45}N_3O_2$: C, 73.68; H, 9.96; N, 9.22. Found: C, 73.56; H, 9.84; N, 9.06.

Registry No.—Cholesteryl iodide, 2930-80-5; cholesteryl chloride, 910-31-6; cholesteryl bromide, 516-91-6; cholesteryl azidoformate, 13084-66-7.

[12] Florisil is a 60–100 mesh magnesium silicate supplied by the Floridin Co., Clarendon, Pa.

[13] Celite is a kieselguhr supplied by the Johns Manville International Corp., New York, N. Y.

[14] For a recent discussion of the adsorption bands due to the antisymmetric stretching vibrations of the azide group in the infrared spectra of organic azides, including azidoformates, see Yu. N. Sheinker, L. B. Senyavina, and V. N. Zheltova, *Dokl. Akad. Nauk SSSR*, **160**, 1339 (1965).

[15] For cholesteryl chloroformate, the corresponding λ_{max} is at 8.65 μ.

The Formation of 1,6-Bis(trichlorosilyl)hexane by the Chloroplatinic Acid Catalyzed Hydrosilylation of 1-Hexyne

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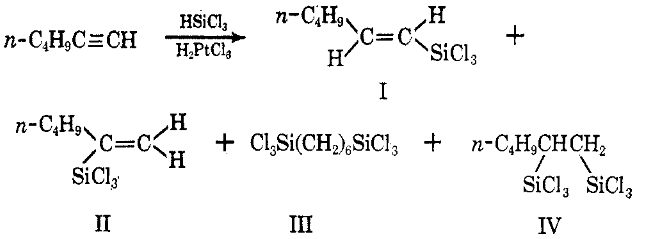
A previous investigation from this laboratory[1] showed that the terminal adduct formed when trichlorosilane is added to monosubstituted acetylenes in the presence of chloroplatinic acid is almost exclusively the *trans* isomer arising from a *cis* addition.

Recently we had occasion to make a detailed study of the addition of trichlorosilane to 1-hexyne catalyzed by chloroplatinic acid. While we have substantiated our earlier findings[1] regarding the stereochemistry of this reaction, we found that, by increasing the severity of the reaction conditions, the usual monoadduct products can be virtually eliminated in favor of diadducts.



Thus, a 1:1 mole ratio of trichlorosilane to 1-hexyne (experiment 2, Table I) and 1 ml of catalyst produced the monoadducts I and II in good yield as the sole products of the reaction. When a 2:1 mole ratio of trichlorosilane to 1-hexyne and a smaller amount of catalyst was used (experiment 1, Table I), monoadducts were still formed exclusively even though the reflux time was increased. Experiments 4–6 (Table I) show that an increase in catalyst concentration[2] seems to favor the formation of the diadducts III and IV. Experiment 3 (Table I) graphically illustrates the effect of reaction time. After 42 hr of reaction, only monoadducts had formed, but after 111 hr, considerable quantities of III and IV had been produced.

The structure of compound I was established by isolating it from the reaction mixture (vpc) and comparing its infrared spectrum with that of an authentic sample. We had synthesized authentic samples of both *cis*- and *trans*-1-trichlorosilyl-1-hexene for this purpose by adding trichlorosilane to 1-hexyne in the presence of benzoyl peroxide.[3] The *trans* isomer could be easily distinguished from the *cis* by virtue of its strong infrared absorption at 10.1 μ.

The structure proof for II rests on its distinctive nmr spectrum. The vinylic protons of this compound possess a small coupling constant (total peak width only 6 cps at half-peak height). Any other arrangement of groups would give a larger coupling constant and a more complicated splitting pattern for the vinylic protons.

In order to establish the structure of compound III, a mixture of the diadducts was isolated from the reaction by distillation and then methylated with methylmagnesium iodide. The product, when analyzed by vpc, showed two peaks in the ratio of 5:95. The material responsible for the major peak was isolated and shown to be 1,6-bis(trimethylsilyl)hexane by its infrared spectrum which corresponded to that of an authentic sample prepared by coupling the di-Grignard reagent derived from 1,6-dibromohexane with trimethylchlorosilane.

[1] R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher *J. Am. Chem. Soc.*, **83**, 4385 (1961).

[2] There are unassessed variables operative in such "platinum-catalyzed" reactions which markedly influence their rate. For instance, in some cases we found freshly prepared catalyst solutions ineffective in causing diadduct formation (monoadduct formation occurred readily), but, after standing 2 days, the same catalyst solution became quite effective in this regard. Hence, it is possible that the catalyst concentration effects noted here are in reality artifacts, being caused by certain other unknown and hence uncontrolled variables. For example, possibly trace amounts of catalyst inhibitors are present whose effects are being swamped out by the increased catalyst concentration.

[3] A reaction known to give a mixture of *cis* and *trans* isomers with a predominance of the former.[1]

TABLE I

CHLOROPLATINIC ACID CATALYZED HYDROSILYLATIONS OF 1-HEXYNE

Expt	H_2PtCl_6[a] ml	Reflux time, hr	I, %	Total monoadducts,[d] %	II, %	III, %	IV, %	Yield, %
1	0.125	24		100				98
2[b]	1	0.5	78		22			92
3[c]	0.25	42	82		18			
3[c]		111		63		20	18	90
4	0.5	20		5		82	14	82
5	0.5	30		2		82	16	81
6	1	4		10		44	40	79

[a] The chloroplatinic acid contained 0.05 g of $H_2PtCl_6 \cdot 6H_2O$/ml in isopropyl alcohol. [b] In this run only, 0.2 mole of trichlorosilane and 0.2 mole of 1-hexyne were used. In all other runs, the molar ratio of trichlorosilane to 1-hexyne was 2:1. [c] Experiment 3 was stopped and analyzed by vpc after 42 hr of refluxing. It was then refluxed for an additional 69 hr. [d] The monoadducts were not analyzed for the percentages of I and II.

TABLE II

NMR SPECTRA OF SOME SILANE ADDUCTS TO 1-HEXYNE[a]

Compound	τ and J values
$CH_3{}^1(CH_2{}^2)_2CH_2{}^3CH^4{=}CH^5SiCl_3$ (*trans*)	9.05 (H^1 multiplet), 8.55 (H^2 multiplet), 7.72 (H^3 multiplet), 3.19 (H^4),[b] 4.16 (H^5);[b] $J_{45} = 18$ cps, $J_{34} = 7$ cps, $J_{35} = 1$ cps
$CH_3{}^1(CH_2{}^2)_2CH_2{}^3CH^4{=}CH^5SiCl_3$ (*cis*)	9.08 (H^1 multiplet), 8.59 (H^2 multiplet), 7.59 (H^3 multiplet), 3.32 (H^4),[b] 4.28 (H^5);[b] $J_{45} = 14$ cps, $J_{34} = 8$ cps, $J_{35} = <1$ cps
$CH_3{}^1(CH_2{}^2)_2CH_2{}^3C(SiCl_3){=}CH_2{}^4$	9.05 (H^1 multiplet), 8.52 (H^2 multiplet), 7.64 (H^3 multiplet), 3.95 (H^4 multiplet);[c] $J_{44} = 6$ cps (half-peak height)
$Cl_3Si(CH_2{}^1)_6SiCl_3$	8.49 (H^1 envelope)
$CH_3{}^1(CH_2{}^2)_3CH^3(SiCl_3)CH_2{}^3SiCl_3$	9.08 (H^1 multiplet), 8.37 (H^2 multiplet), 8.55 (H^3 multiplet)
$[(CH_3{}^1)_3SiCH_2{}^2(CH_2{}^3)_2]_2$	9.90 (H^1 singlet), 9.40 (H^2 envelope), 8.60 (H^3 envelope)

[a] These spectra were all determined in carbon tetrachloride solution using a Varian A-60 instrument. In each spectrum the peak areas were consistent with the proton assignments made. [b] The vinylic protons in this compound gave a clearly resolved AB splitting pattern with each peak of the pattern further split into a triplet by the allylic methylene protons. [c] This multiplet appeared to be a poorly resolved AB pattern.

The structure of diadduct IV was established in a similar fashion by matching its infrared spectrum with that of an authentic sample. The latter was obtained by the addition of trichlorosilane to 2-trichlorosilyl-1-hexene in the presence of benzoyl peroxide. In Table

$$\mathrm{II} \xrightarrow[\text{benzoyl peroxide}]{HSiCl_3} \mathrm{IV}$$

II are listed the nmr spectra of all the compounds which were characterized in this work. It seems highly likely that diadduct IV is formed principally by the addition of another molecule of trichlorosilane to monoadduct II. An examination of the data listed for ex-

$$\mathrm{II} \xrightarrow{HSiCl_3} \mathrm{IV}$$

periment 3 (Table I) lends some support to this hypothesis. After 42 hr of reaction, 18% of II had formed and none of IV. After 111 hr, 18% of IV had been produced. Likewise, the formation of diadduct III may be regarded as analogous to the formation of terminal adducts in the chloroplatinic acid catalyzed hydrosilylation of internal olefins which has been observed by several workers.[4-6]

$$\mathrm{I} \xrightarrow{HSiCl_3} \mathrm{III}$$

Experimental Section

Hydrosilylation of 1-Hexyne.—A three-necked flask was fitted with a reflux condenser and a thermometer and the entire system was flushed with dry nitrogen and flamed out. When the flask had cooled to room temperature, 8.2 g (0.10 mole) of 1-hexyne and 20 ml (0.20 mole) of trichlorosilane were mixed in the flask. The desired volume of a solution of chloroplatinic acid in isopropyl alcohol (see Table I) (0.05 g of $H_2PtCl_6 \cdot 6H_2O$/ml) was introduced with a syringe and the reaction mixture was then refluxed under a positive pressure of dry nitrogen.

The unreacted trichlorosilane and 1-hexyne were removed by distillation at atmospheric pressure. Vacuum distillation of the residue gave monoadducts, 50–60° (4.0 mm), and diadducts, 110–120° (2.5 mm). The fractions were analyzed by vpc. In all runs, more than 95% of the 1-hexyne was accounted for either by recovery or as adducts. The results are summarized in Table I.

Analysis of Products.—The monoadducts could be separated using a 15 ft × 0.25 in. stainless steel column packed with 23% QF-1 on 60–80 mesh Chromosorb-P at 160° with a flow of 60 ml of helium/min, compound II eluting in 11.1 min and I eluting in 13.5 min. In the monoadduct fractions which were analyzed, traces of other materials were observed, but there was never enough of these compounds to characterize. The diadducts did not elute from this column. The diadducts could be analyzed on a 5 ft × 0.25 in. stainless steel column packed with 25% SF-96 on 60–80 mesh Chromosorb-P at 200° with a flow of 60 ml of helium/min. The monoadducts (I and II) eluted in 1.6 min while IV and III eluted in 4.3 and 7.2 min, respectively.

***cis*- and *trans*-1-Trichlorosilyl-1-hexene.**—Trichlorosilane (135.4 g, 1 mole), 1-hexyne (41.0 g, 0.5 mole), and benzoyl peroxide (12.1 g, 0.05 mole) were added to 500 ml of cyclohexane and the solution held at reflux in a closed system (mercury trap) for 69

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(4) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(5) J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958); **83**, 1351 (1961).

(6) T. G. Selin and R. West, *ibid.*, **84**, 1863 (1962).

(7) Previous work[1] had demonstrated that such peroxide-catalyzed reactions give predominantly the *cis* isomer.

hr. Excess starting materials and solvent were then removed by distillation under aspirator vacuum and the residue was distilled on a Todd apparatus. A total of 28.3 g (26%) of *cis*- and *trans*-1-(trichlorosilyl)-1-hexene boiling at 58–63° (5 mm) was obtained. A partial separation of the two isomers was accomplished by distillation. The cut (21.6 g) boiling at 58–59° (5 mm) was comprised of 70% of the *cis* isomer.[7] Complete separation of the two isomers was readily achieved by vpc (10-ft QF-1 column at 110°). The *trans* isomer possessed a strong infrared band at 10.1 μ which was absent in the spectrum of the *cis* isomer. The nmr spectra of both isomers are listed in Table II.

Anal. Calcd for $C_6H_{11}Cl_3Si$ (*cis* and *trans*): C, 33.12; H, 5.10; Cl, 48.89. Found (*cis*): C, 33.25; H, 5.06; Cl, 49.29. Found (*trans*): C, 33.29; H, 4.97; Cl, 49.22.

In experiment 1 (Table I), compound I was isolated from the reaction mixture by vpc. Its infrared and nmr spectra were identical with the *trans*-1-trichlorosilyl-1-hexene prepared above.

2-Trichlorosilyl-1-hexene (II).—This monoadduct was collected by vpc from the products of experiment 1. Its structure was assigned on the basis of its nmr spectrum (Table II).

Anal. Calcd for $C_6H_{11}Cl_3Si$: C, 33.12; H, 5.10; Cl, 48.89; Si, 12.89. Found: C, 33.27; H, 5.25; Cl, 48.59; Si, 12.89.

1,6-Bis(trichlorosilyl)hexane (III).—A pure sample of this compound was collected by vpc from the products of experiment 3 (Table I). Its nmr spectrum is reported in Table II.

Anal. Calcd for $C_6H_{12}Cl_6Si_2$: C, 20.41; H, 3.42; Cl, 60.25. Found: C, 20.60; H, 3.36; Cl, 60.34.

1,6-Bis(trimethylsilyl)hexane.—A 500-ml three-necked flask fitted with a condenser, stirrer, and dropping funnel was flamed out and then cooled in a dry nitrogen atmosphere. Magnesium (12.0 g, 0.5 g-atom) in 150 ml of anhydrous diethyl ether was added to the flask followed by the slow addition of 36 g (0.25 mole) of 1,6-dibromohexane. The mixture was refluxed for 5 hr after the addition was complete. Trimethylchlorosilane (54.3 g, 0.5 mole) was then added slowly and the mixture was heated for 7 hr. It was then hydrolyzed with 3 *N* hydrochloric acid and worked up as usual. After solvent removal, the residue was distilled. A very pure center cut (10.5 g) was collected boiling sharply at 104° (7 mm). This material gave only one peak when analyzed by vpc (QF-1 column) and was identical in every respect (retention time, infrared, and nmr spectrum) with the methylated sample obtained below.

Anal. Calcd for $C_{12}H_{30}Si_2$: C, 62.61; H, 13.05. Found: C, 62.70; H, 13.29.

A portion (18.0 g, 0.05 mole) of the diadduct distillation cut, bp 125–126° (2.3 mm), was treated with methylmagnesium iodide prepared from 0.3 mole of methyl iodide and 0.3 g-atom of magnesium. After 4 hr of refluxing followed by the usual work-up, there was obtained 9.7 g (88%) of 1,6-bis(trimethylsilyl)hexane boiling at 121–122° (23 mm). Analysis of this sample showed that it was 95% pure. There was only one contaminant present in 5% quantity. A small sample of the major product was collected by vpc and had identical properties with the authentic sample prepared above.

Anal. Calcd for $C_{12}H_{30}Si_2$: C, 62.61; H, 13.04. Found: C, 62.75; H, 13.26.

1,2-Bis(trichlorosilyl)hexane (IV).—In a 10-ml conical flask, 1.4 g (6.5 mmoles) of 2-trichlorosilyl-1-hexene,[8] 1.3 ml (13 mmoles) of trichlorosilane, 2.1 ml of cyclohexane, and 0.105 g (0.434 mmole) of benzoyl peroxide were refluxed for 29 hr. Distillation of the product gave 1.4 g (61%) of 1,2-bis(trichlorosilyl)hexane boiling at 105–107° (2.2 mm). This same material, as adjudged by the identity of its retention time (vpc) and infrared spectrum, was collected by vpc as the more volatile diadduct from experiment 3 (Table I).

Anal. Calcd for $C_6H_{12}Cl_6Si_2$: C, 20.41; H, 3.42; Cl, 60.25. Found: C, 20.45; H, 3.41; Cl, 60.50.

Registry No.—I (*trans*), 13095-00-6; I (*cis*), 13083-92-6; II, 13083-93-7; III, 13083-94-8; IV, 13083-95-9; 1,6-bis(trimethylsilyl)hexane, 13083-96-0; 1-hexyne, 693-02-7.

Acknowledgment.—The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

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[8] This material was collected by preparative scale vpc from a mixture of the monoadduct fractions of experiments 1, 3, and 6 (Table I).

Organometalloid Azides. IV. Preparation and Reactions of N,N′-[*p*-Arylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic azides)[1]

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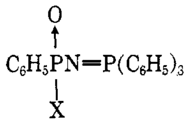
Received January, 27, 1967

It has been previously demonstrated that phenylphosphonic diazide I reacts with arylenebis(*t*-phosphines) to yield low molecular weight polyphosphoranes which had promising thermal and hydrolytic stabilities.[2] However, owing to the extreme shock, thermal, and hydrolytic sensitivities of I, it was hazardous to purify or handle large quantities of I for use in polymerization studies. Subsequently, it was further demonstrated that phenylphosphonic diazide reacted with triphenylphosphine in a clearly defined, two-step reaction. The intermediate, azidophosphorane IIa, was readily isolated in both high yield and purity.[2] These results

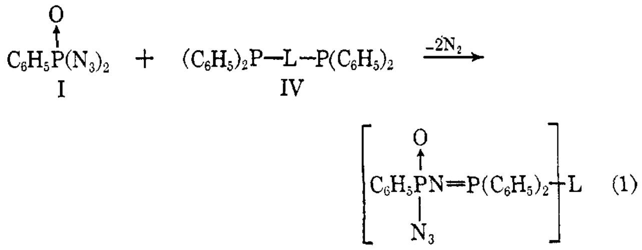


$$C_6H_5\overset{\overset{O}{\uparrow}}{P}(X)N{=}P(C_6H_5)_3$$

IIa, X = N_3
b, X = Cl

suggested that arylene-linked bis(azidophosphoranes) might be valuable intermediates for use in the syntheses of polyphosphoranes. In this paper, we now wish to report the syntheses and properties of such bis(azidophosphoranes), N,N′-[*p*-arylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic azides) (III).

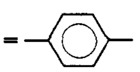
The slow addition of 1 mole of bis(tertiary phosphine) IV to a solution containing at least 2 moles of phenylphosphonic diazide (I) so as to maintain the reaction temperature in the range 25–30° gave good yields of the product bis(azidophosphoranes) III (eq 1). While



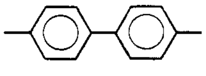
$$\underset{\text{I}}{C_6H_5\overset{\overset{O}{\uparrow}}{P}(N_3)_2} + \underset{\text{IV}}{(C_6H_5)_2P{-}L{-}P(C_6H_5)_2} \xrightarrow{-2N_2} \left[C_6H_5\overset{\overset{O}{\uparrow}}{\underset{\underset{N_3}{|}}{P}}N{=}P(C_6H_5)_2\right]_2 L \quad (1)$$

III

a, L =



b, L =



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[1] (a) The research was supported by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, under Contract AF 33(615)-3570. (b) Presented in part at the First Annual Western Regional Meeting of the American Chemical Society, Los Angeles, Calif., Nov 1965. (c) Part III of this series: R. A. Baldwin, C. O. Wilson, Jr., and R. I. Wagner, *J. Org. Chem.*, **32**, 2172 (1967).

[2] R. A. Baldwin, *J. Org. Chem.*, **30**, 3866 (1965).