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STUDIES IN ORGANOSILICON CHEMISTRY
XLVIII. THE ADDITION OF TRICHLOROSILANE TO MYRCENE*

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SUMMARY

The addition of trichlorosilane to the naturally occurring terpene, myrcene, in the presence of chloroplatinic acid catalyst, was studied. A set of reactions was run at ambient pressure using various mole ratios of myrcene to trichlorosilane, yielding three products: 1,2- and 1,4-monoadducts and a 1,2-, 3,4-diadduct. Of the two monoadduct products, the 1,2-adduct was apparently favored. Chemical analysis in conjunction with IR and NMR analysis (the latter to be published at a later time) showed the occurrence of terminal addition of the silicon atom at the unsaturated sites. The triadduct was synthesized from the diadduct at 105° and elevated pressure. Terminal addition of the silicon atom occurred through bond isomerization based on a π-complex mechanism. Thus, the three double bonds of myrcene exhibited a tendency to undergo attack by the trichlorosilane in the following order: $RCH{=}CH_2 > RR'C{=}CH_2 > R_2C{=}CHR'$ (isopropylidene).

INTRODUCTION

The addition of silicon hydrides to naturally occurring cyclic terpenes was first investigated by Goldblatt and Oldroyd[1]. They reported that terpenes having at least one non-aromatic double bond add halosilicon hydrides, in the presence of peroxides, yielding silicon hydride/terpene adducts. Addition products from silicon hydrides (trichloro- and methyldichlorosilanes) and terpenes (2- and 2(10)-pinenes, camphene and *p*-mentha-1,8-dienes) in the presence of peroxides (benzoyl and acetyl) were isolated. Further investigations by Calas and Frainnet[2,3] confirmed the fact that trichlorosilane adds to 2(10)-pinene in the presence of peroxides, but with ring opening to give the monoaddition product, 7-(trichlorosilyl)-*p*-menth-1-ene (I), by a typical free radical mechanism. Under the influence of UV radiation, Frainnet[4,5]

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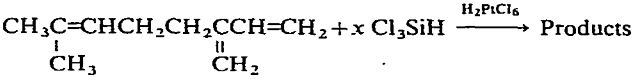
also showed that addition occurs to 2(10)-pinene to yield (I) and a small quantity of the diadduct, 2,7-bis(trichlorosilyl)-*p*-mentane. 2-Pinene and trichlorosilane also react under similar conditions to give mono- and diaddition products. The addition of trichlorosilane to *p*-mentha-1,8-diene, in the presence of UV radiation, was reported by Calas[6] to have yielded primarily a monoaddition product, 9-(trichlorosilyl)-*p*-menth-1-ene (II) and a small quantity of a diaddition product, 2,9-bis(trichlorosilyl)-*p*-menthane (III). In a subsequent publication, Valade and Calas[7] showed that two monoaddition products, (II) and 2-(trichlorosilyl)-*p*-menth-8-ene and the diadduct (III) were formed.

RESULTS

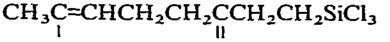
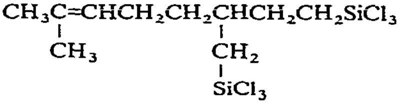
We wish to report the addition of trichlorosilane to the naturally occurring, aliphatic open chain terpene, myrcene (7-methyl-3-methylene-1,6-octadiene). This compound is unique since it contains three distinct types of unsaturated linkages; vinyl, terminal methylene and isopropylidene, of which the former two are conjugated. Several reactions were run at ambient pressure where the mole ratio of myrcene to trichlorosilane was systematically varied. An attempt was made to saturate the available olefinic sites in a stepwise manner with the isolation of intermediate addition products using chloroplatinic acid as the catalyst, very often referred to as Speier's Catalyst[8]. Experimental details and results are summarized in Table 1.

TABLE 1



$$CH_3\underset{\overset{|}{CH_3}}{C}{=}CHCH_2CH_2\underset{\overset{\|}{CH_2}}{C}CH{=}CH_2 + x\,Cl_3SiH \xrightarrow{H_2PtCl_6} \text{Products}$$

ADDITION OF TRICHLOROSILANE TO MYRCENE (AMBIENT PRESSURE)

Run no.	Mole ratio $\frac{\text{myrcene}}{Cl_3SiH}$	H_2PtCl_6 conc. $\frac{\text{mole catalyst}}{\text{mole myrcene}}$	Temp. (°C)	Time (h)	Product(s) isolated	Yield (%)
1	1/1	3.8×10^{-5}	55–90	4	 $CH_3\underset{\overset{|}{CH_3}}{C}{=}CHCH_2CH_2\underset{\overset{\|}{CH_2}}{C}CH_2CH_2SiCl_3$ (IV)	40.6
					 $CH_3\underset{\overset{|}{CH_3}}{C}{=}CHCH_2CH_2\underset{\overset{|}{\underset{\overset{|}{SiCl_3}}{CH_2}}}{CH}CH_2CH_2SiCl_3$ (V)	19.0
2	1/1	2.0×10^{-5}	55–90	4	(IV) and (V)	39.4, 18.4
3	1/1	1.1×10^{-5}	55–89	4	(IV) and (V)	40.1, 17.3
4	1/2	5.4×10^{-5}	39–90	6	 $CH_3\underset{\overset{|}{CH_3}}{C}{=}CHCH_2CH_2\underset{\overset{|}{CH_3}}{C}{=}CHCH_2SiCl_3$ (VI)	6.4
					and (V)	48.2
5	1/2	2.6×10^{-5}	36–90	6	(VI) and (V)	7.6, 46.0
6	1/3.5	6.5×10^{-5}	37–54	35	(VI) and (V)	6.5, 44.4

To favor the formation of monosilyl addition product, the first set of three experiments, runs 1, 2, and 3 were conducted at a 1/1 mole ratio of myrcene to trichlorosilane at various concentrations of catalyst. Catalyst concentration had very little, if any effect upon yields or relative ratios of the two products obtained. Quantitative chemical analyses for silicon and chloride showed them to be a monotrichlorosilyl adduct (IV) and a ditrichlorosilyl adduct (V) of myrcene. IR analysis of the monoadduct showed that the C–H out-of-plane deformation bands at 990 and 902 cm^{-1}, assigned to the vinyl unsaturation found in the myrcene spectrum, had disappeared, but that the C=C stretching band (1670 cm^{-1}) for the isopropylidene and terminal methylene (1647 cm^{-1}) and the C–H out-of-plane deformation bands for terminal methylene (892 cm^{-1}) and for the isopropylidene group (827 cm^{-1}) remained. In addition the stretching bands at 1638 and 1595 cm^{-1}, due to the conjugation effect between the vinyl and terminal methylene groups, had also disappeared. The shoulder band at 1395 cm^{-1} was assigned to the C–H deformation of the SiC–H linkage. IR data are summarized in Table 2. The suspected terminal addition of the silicon atom to the vinyl group was verified by NMR analysis. It was found that

TABLE 2

SUMMARY OF IR DATA OF MYRCENE AND ITS TRICHLOROSILYL DERIVATIVES

Group	Attributed to	IR absorption bands (cm^{-1})				
		Myrcene	(IV)	(V)	(VI)	(VII)
$-CH=CH_2$ (vinyl)	C–H stretching	3080 m				
$R_1R_2C=CH_2$ (terminal methylene)		3080 m	3080 w	Missing	Missing	Missing
CH_3-, $-CH_2-$	C–H stretching	2965–2870 s	2975–2880 s	2970–2880 s	2970–2880 s	2970–2890 s
$R_1R_2C=CH_2$	Overtone of CH_2 out-of-plane deformation	1785 w	1783 w	Missing	Missing	Missing
$R_1R_2C=CHR_3$ (isopropylidene)	C=C stretching	1667 w	1670 w	1665 w	1660 w	Missing
$-CH=CH_2$, $R_1R_2C=CH_2$	C=C stretching (conjugation)	1638 w, 1595 s	Missing	Missing	Missing	Missing
$R_1R_2C=CH_2$	C=C stretching (non-conjugation)		1647 m	Missing	Missing	Missing
CH_3-, $-CH_2-$	C–H deformation (asymmetric)	1448 m	1448 m	1451 m	1452 m	1465 m
$Si-CH_2$	C–H asymmetric deformation influenced by Si–C linkage		1395 w (sh)	1395 m	1395 m (sh)	1398 m
CH_3-	C–H deformation (symmetric)	1377 m	1380 m	1377 m	1385 m	1385 m
$-CH=CH_2$	C–H out-of-plane deformation	990 s 902 s	Missing	Missing	Missing	Missing
$R_1R_2C=CH_2$	C–H out-of-plane deformation	893 s	892 s	Missing	Missing	Missing
$R_1R_2C=CHR_3$[a]	C–H out-of-plane deformation	823 w	823 w	828 w	815 w (temporary)	Missing
Si–Cl	Stretching	Missing	Below 800	Below 800	Below 800	Below 800

[a] Infrared absorption bands due to this relatively symmetrical group are very weak and somewhat inconsistent especially for the C–H out-of-plane deformations. Due caution must be exercised in their interpretation.

only protons from two distinct methyl groups* (from the isopropylidene group) at 1.57 and 1.65 ppm were evident with a pattern similar to that found in myrcene. If non-terminal addition had occurred, three distinct methyl peaks would be evident or at least it would be suspected that the original two methyl peak patterns found in myrcene would be altered. We intend to discuss this more completely in a subsequent publication.

IR analysis of the diadduct showed that not only were the peaks assigned to the vinyl unsaturation missing, but also the bands assigned to the terminal methylene at 3080, 1783, 1647 and 892 cm^{-1} [previously assigned for (IV)] were also gone. There still remained the 1665 cm^{-1} absorption band for the C=C stretching frequency and the 828 cm^{-1} band for the C–H out-of-plane deformation for the isopropylidene group. The weak shoulder band at 1395 cm^{-1}, assigned originally to the C–H deformation of the SiC–H linkage in the monoadduct, was present as a medium strength band due to two SiC–H linkages in the diadduct. See Table 2. Further verification of structure (V) will be found in a subsequent publication covering NMR data with related interpretation.

Two products were isolated from the reaction between myrcene and trichlorosilane, runs 4 and 5, a mono- and a diadduct. The diadduct was identified as compound (V). The monoadduct was found to be a 1,4-addition product of myrcene, designated in Table 1 as compound (VI). No 1,2-addition product, compound (IV), was found. Apparently, any (IV) which was formed reacted further with additional trichlorosilane through its available terminal methylene group to give the diadduct, compound (V). The generated internal double bond in compound (VI) resisted the addition of trichlorosilane and, therefore, remained intact. A very small quantity of this material (VI) was isolated, indicating that trichlorosilane under conditions of the test preferentially added in a 1,2-manner to the vinyl linkage with further addition to form the identified diadduct. Others have reported the isolation of 1,4-monoaddition products in analogous systems. Bailey and Pines[9] investigated the addition of trichlorosilane to butadiene and obtained primarily the 1,4-adduct. Similarly, Shiihara, Hoskyns and Post[10] showed that trichlorosilane and other silicon hydrides add to isoprene to give only the 1,4-addition product. Mamedaliev *et al.*[11] reported in addition the 1,2-product. With chloroprene and trichlorosilane, only the 1,4-product was obtained.

The IR spectrum of compound (VI) showed that the previously assigned bands for the vinyl and terminal methylene groups were now missing. The bands at 1660 and 815 cm^{-1} normally assigned to the isopropylidene group had been slightly strengthened by the additional internal double bond found in compound (VI). The C–H symmetrical deformation band at 1385 cm^{-1}, assigned to the terminal methyl groups, was somewhat broader than in the previous spectrum, indicating the presence of an additional methyl group which would be consistent with the assigned structure. IR data are summarized in Table 2 and NMR data will be published in the near future.

Run 6 was conducted with an excess of trichlorosilane. Results similar to those obtained for runs 4 and 5 were noted with no evidence of triadduct formation. The isopropylidene group, as well as the generated internal double bond in compound (VI), resisted the addition of trichlorosilane under the experimental conditions described.

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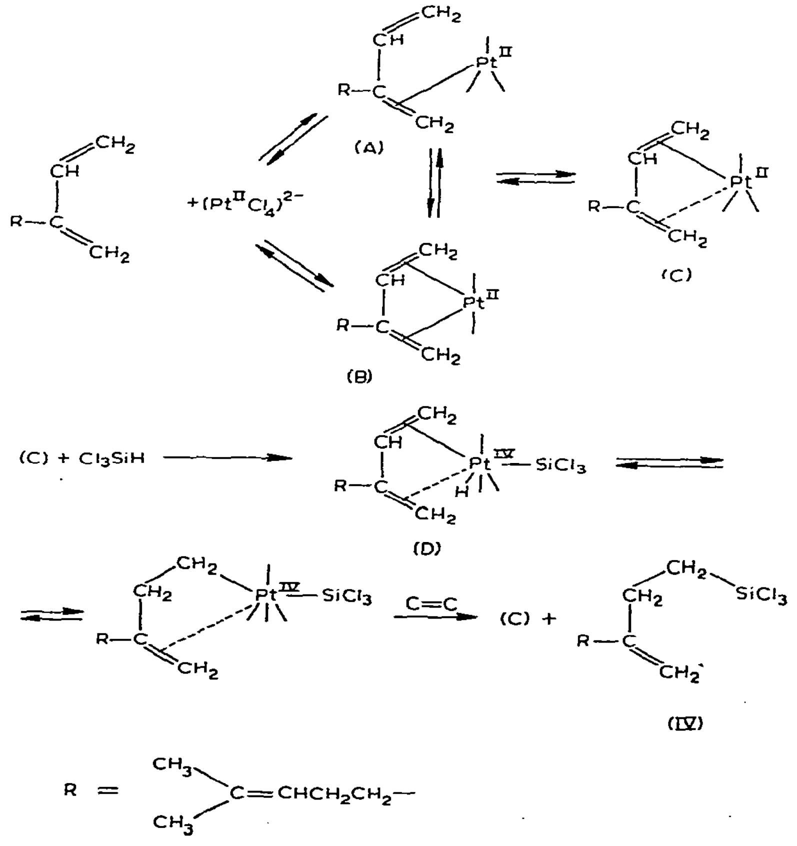
* The NMR spectrum was run on the trimethylsilyl derivative.

DISCUSSION

Hydrosilation reactions under the influence of chloroplatinic acid have been reported in numerous publications with various detailed explanations[8-17]. Chalk and Harrod[18] were the first to suggest a mechanism for the coordination-catalyzed hydrosilation of olefins which was later supported by other authors[19,20]. They reported that hydrosilation reactions are more dependent on the nature of the substrate than on the nature of the catalyst. Thus, a platinum(II)–olefin complex such as $[(C_2H_4)PtCl_2]_2$ was found to yield similar silyl end products to those resulting from the catalytic influence of chloroplatinic acid. The catalyst responsible for the initial formation of the complex involves the lower oxidation state of platinum and with chloroplatinic acid, platinum(II) is probably formed by reduction with silicon hydride[13-15,21]. Their mechanism makes possible an unlimited series of consecutive double bond shifts via the alkyl chain resulting in the formation of terminal addition products.

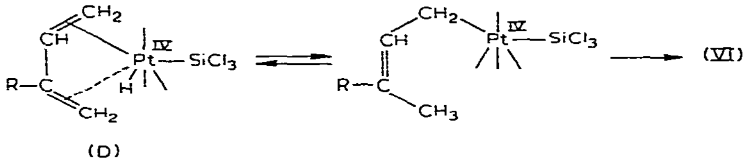
The following mechanism is proposed for the formation of the 1,2-monoaddition, terminal silyl product:

$$(Pt^{IV}Cl)^{2-} \xrightarrow{SiH} (Pt^{II}Cl_4)^{2-}$$



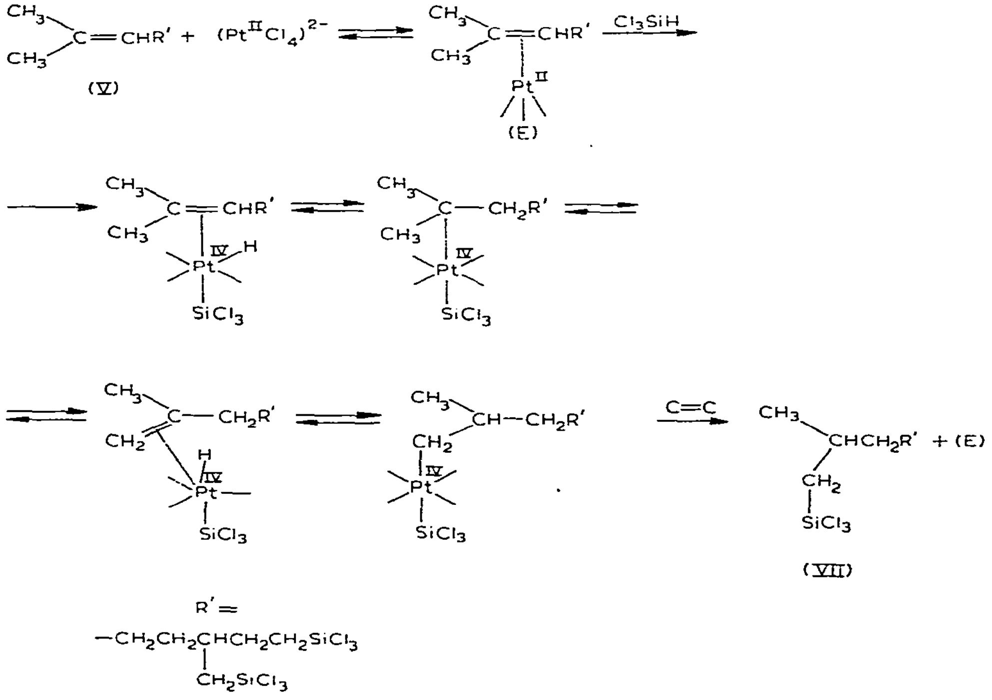
It is suggested that the π complex (C) is primarily responsible for product formation based on published work[15,22,23,30] reporting that coordination ability of olefins decreases with increasing number of substituents about its double bond due to steric effects. Some weaker interaction with the terminal methylene double bond is reasonably evident.

Essentially the same reasoning can be used to describe the formation of the 1,4-monoadduct. The projected octahedral π complex (D) can be rearranged by the nucleophilic attack of the hydride ion at the terminal carbon of the methylene group with appropriate electron shifts to form the observed 1,4-product (VI).



The formation of the diadduct (V) seems to follow a stepwise reaction path primarily through the complex activation of the 1,2-mono derivative. The interaction of the platinum center with the isopropylidene group[24] is also a strong possibility. The isolation of some diadduct during reaction of equal molar quantities of myrcene and silane (runs 1–3) suggests its formation could also proceed through further hydrosilation of a labile 3,4-monoadduct generated through a π complex as (A) or (B). It is of our opinion that both reaction paths are operable.

Attempted saturation of the isopropylidene group in preference to the vinyl and/or methylene olefinic bonds or total saturation of the myrcene molecule to yield



a trisilyl adduct was not successful under conditions of ambient pressure and reflux temperatures. Branching at the isopropylidene bond impeded strong π complex formation due to steric and/or electronic factors as previously mentioned.

The addition of trichlorosilane to the isopropylidene group of the diadduct (V) was achieved under pressure at 105° during 24 h in a Carius tube. Heat was required since the isomerization reactions are usually slow and the equilibrium mixture of isomers at low temperatures is lean in vinyl groups[16,20,25,26].

IR analyses of the resultant triadduct (VII) showed that the isopropylidene group was saturated. The fairly medium-strong bond at 1397 cm^{-1} was assigned to the three Si–CH linkages in the triadduct. NMR analyses, to be published in the near future, supported the presence of terminal silyl addition, brought about by bond isomerization according to the original work reported by Chalk and Harrod[18].

EXPERIMENTAL

A. Ambient pressure reactions

Addition of trichlorosilane to myrcene (7-methyl-3-methylene-1,6-octadiene). Over a 15-min period, 49.8 g (0.37 mole) of trichlorosilane was added to 50.0 g (0.37 mole) of myrcene and 0.14 ml of 0.1 *M* chloroplatinic acid catalyst ($H_2PtCl_6 \cdot 6\ H_2O$) in isopropyl alcohol (3.8×10^{-5} mole catalyst/mole myrcene) in a 200 ml flash. The system was refluxed at a rate which brought the pot temperature from 55 to 90° in 4 h. Fractionation yielded two significant fractions: fraction one, 48.4 g, b.p. 69.0–71.1°(0.1 mm); fraction two, 17.5 g, b.p. 129.4–131.0°(0.1 mm). Refractionation of one yielded (IV), 40.5 g (40.6% yield), b.p. 70.0–70.7°(0.1 mm) (uncorrected). (Found: Cl, 39.01, 38.93; Si, 10.19, 10.08. $C_{10}H_{17}Cl_3Si$ calcd.: Cl, 39.15; Si, 10.34%.) Refractionation of two yielded (V), 14.2 g (19.0% yield based on trichlorosilane), b.p. 130.2–130.8°(0.1 mm)(uncorrected). (Found: Cl, 52.13, 52.05; Si, 13.66, 13.65. $C_{10}H_{18}Si_2Cl_6$ calcd.: Cl, 52.25; Si, 13.80%.)

The reaction was repeated when 69.9 g (0.52 mole) of trichlorosilane was added to 35.0 g (0.26 mole) of myrcene and 0.14 ml of catalyst (5.4×10^{-5} mole catalyst/mole myrcene) over a 20-min period. The system was refluxed at a rate such that the pot temperature increased from 39 to 90° in 6 h. This fractionation also yielded two significant fractions: fraction one, 8.0 g, b.p. 66.5–68.3°(0.1 mm); fraction two, 56.4 g, b.p. 129.5–131.5°(0.1 mm). Refractionation of one yielded (VI), 4.5 g (6.4% yield), b.p. 67.0–67.6°(0.1 mm). (Found: Cl, 38.99, 38.84; Si, 10.19, 10.17. $C_{10}H_{17}Cl_3Si$ calcd.: Cl, 39.15; Si, 10.34%.) Refractionation of two yielded (V), 50.4 g (48.2% yield), b.p. 130.3–131.4°(0.1 mm) (uncorrected). (Analysis comparable to above.)

Over a 30-min period, 81.3 g (0.60 mole) of trichlorosilane added to 23.0 g (0.17 mole) of myrcene and 0.11 ml of catalyst (6.5×10^{-5} mole catalyst/mole myrcene) in a 200 ml flask and refluxed for 35 h as the temperature of the refluxing mixture increased from 37 to 54°. Some loss of trichlorosilane from the refluxing system was evident. Fractionation followed by refractionation yielded (VI), 3.0 g (6.5% yield) and (V), 30.4 g (44.0% yield). Boiling points and analysis are comparable to above.

B. Pressure reaction

Addition of trichlorosilane to trichloro{7-methyl-3[(trichlorosilyl)methyl]-6-octenyl}silane (V). To a chilled (methylene chloride/dry ice bath), nitrogen purged, 19 mm ID × 60 cm Carius tube, were added 7.7 g (0.06 mole) trichlorosilane, 20.0 g (0.05 mole) (V) and 0.10 ml of catalyst [2.0×10^{-4} mole catalyst/mole (V)] sealed and annealed. The tube was heated in an explosion proof electric tube furnace for two hours at 60° and 24 h at 105°. Upon completion of the heating cycle, fractional distillation yielded only one isolable product, (VII), 16.8 g, b.p. 174.3–176.5°(0.3 mm). Refractionation yielded 13.1 g (48.8% yield), b.p. 174.1–174.8°(0.3 mm), uncorrected. (Found: Cl, 58.49, 58.40; Si, 15.40, 15.35. $C_{10}H_{19}Cl_9Si_3$ calcd.: Cl, 58.81; Si, 15.53%.)

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