usual to give 10.0 g. (73%) of 3,4,5-trimethylphenol,[17] m.p. 105–107°. Sublimation afforded a polymorphic form, m.p. 58–60°, which easily went to the higher melting form on recrystallization from Skellysolve B.

4-Trichloromethyl-3,4,5-trimethyl-2,5-cyclohexadienone (IX).—In a typical run, a solution of 2.72 g. of 3,4,5-trimethylphenol in 50 ml. of carbon tetrachloride was added to a slurry of 5.32 g. of anhydrous aluminum chloride[18] in 80 ml. of carbon tetrachloride and 20 ml. of carbon disulfide held at −20 ± 5°. After 4.5 hr. at this temperature, the deep red mixture was poured on iced acid and worked up as usual to yield 1.2 g. (24%) of IX, as pale orange crystals, m.p. 113–115°. The colorless analytical sample, m.p. 117.0–117.5° (infrared band at 5.98 μ), was obtained on recrystallization from Skellysolve B with little loss. From alkaline washes of the reaction mixture, 74% of starting 3,4,5-trimethylphenol was recovered. In a similar run, except that the reaction was held at −20 ± 5° for 30 hr., the yield of pure IX was 62%, but only 11% of starting phenol was recovered.

Anal. Calcd. for $C_{10}H_{11}Cl_3O$: C, 47.4; H, 4.4; Cl, 42.0. Found: C, 47.6; H, 4.4; Cl, 41.9.

The red 2,4-dinitrophenylhydrazone, m.p. 163–165° dec., was readily formed.

Anal. Calcd. for $C_{16}H_{15}Cl_3N_4O_4$: N, 12.9. Found: N, 12.8.

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[17] K. von Auwers and F. Wieners, *Ber.*, **58**, 2815 (1925).

[18] Supplied by the Ohio-Apex Division, Food Machinery and Chemical Corp.

The Addition of Silicon Hydrides to Olefinic Double Bonds. X. Addition to Phenylalkenes. The Nuclear Magnetic Resonance Proton Spectra of (Phenylalkyl)silanes

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Received March 2, 1964

The addition of certain silicon hydrides to phenylalkenes of the formula $Ph(CH_2)_nCH{=}CH_2$ (I) or $PhCH{=}CH(CH_2)_nH$ (II) (n = 0 to 4) with chloroplatinic acid as the catalyst leads in each case to two products: A, $Ph(CH_2)_{n+2}SiMe_xY_{3-x}$, and C, $PhCH(SiMe_xY_{3-x})(CH_2)_{n+1}H$. Examples were studied with Y = Cl, F, or Me_3SiO and x = 0, 1, 2, or 3. The relative amounts of A to C in each case depends upon the nature of Y and the values of x and n. Substituents on the phenyl group in styrene also influence the ratio of products of type A to type C. The H^1 n.m.r. spectra of (phenylalkyl)silanes were studied.

The addition of chlorosilicon hydrides to the double bond of a linear olefin is catalyzed by chloroplatinic acid to form n-alkylsilanes, regardless of the original position of the double bond in the olefin. Pentene-2[1] or heptene-3[2] gave n-pentyl- or n-heptylsilanes exclusively.

Certain substituted olefins formed more than one adduct when the olefinic double bond was conjugated with another double bond. For example, styrene formed both (1- and 2-phenylethyl)chlorosilanes[3] and methyl acrylate formed the 2- and the 3-chlorosilylpropionic esters with either chloroplatinic acid[1] or platinum on carbon[4] as the catalyst. Fluorosilicon hydrides were found to act much like chlorosilicon hydrides in their addition to styrene.[5] The only nonconjugated, unsaturated compounds known to have made nonterminal adducts with halosilicon hydrides have been compounds such as cyclohexene[1] or methylcyclohexene.[6,7]

Recently Petrov, *et al.*,[8] reported that RCl_2SiH (R = Me or Et) with alkenylbenzenes, $Ph(CH_2)_nCH{=}CH_2$ (n = 0, 1, and 2), makes isomeric adducts A, $Ph(CH_2)_{n+2}SiCl_2R$, and B, $Ph(CH_2)_nCHCH_3(SiCl_2R)$, with chloroplatinic acid or platinum or carbon as catalysts. Trichlorosilane, on the other hand, was reported to form only terminal adducts, $Ph(CH_2)_{n+2}SiCl_3$.

In this laboratory the formation of so unexpected a series as B was of interest as the first examples of nonterminal addition of a chlorosilicon hydride to a nonconjugated terminal double bond. The addition of chlorosilicon hydrides to alkenylbenzenes was, therefore, re-examined using chloroplatinic acid in isopropyl alcohol as the catalyst.

Styrene, allylbenzene, and 4-phenylbutene-1 each formed two isomeric adducts with chlorosilicon hydrides and chloroplatinic acid at 100° in sealed tubes for 16 hr. (see Table I). The silyl group in the adducts was attached either to the terminal position, as in A, or, contrary to the paper by Petrov, *et al.*,[8] in the position α to phenyl, as in C [$({\equiv}SiCHPh(CH_2)_nCH_3)$]. No other isomers were observed. Trichlorosilane formed both the A and C series of adducts.

The formation of A was favored in every example, but the ratio of A/C was dependent upon the silane and increased in the series Cl_3SiH < Cl_2MeSiH < $ClMe_2SiH$. Dimethylchlorosilane tended most strongly to form A and was least influenced by tetrahydrofuran and by ratio of reagents. The effect of tetrahydrofuran during the reaction was impressive with styrene and trichlorosilane or methyldichlorosilane, but was scarcely detectable with styrene and dimethylchlorosilane. The use of a solvent in such a system to influence the ratio of products has been noted by Pike and Borchert.[9] As n increased and the double bond became more isolated from the benzene ring, more of the terminal adduct formed in each case.

Excess allylbenzene or 4-phenylbutene became mixtures of isomers very rich in *trans*-1-phenylpropene or *trans*-1-phenylbutene. The formation of these isomers was so favored that for a time we thought the isomerization might be stereoselective. However, isomerization of the olefins with sodium on alumina gave nearly identical mixtures, equally favoring the *trans*-1-phenylalkenes. Haag and Pines[10] have shown that

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

[2] J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958).

[3] J. W. Ryan and J. L. Speier, *J. Org. Chem.*, **24**, 2052 (1959).

[4] L. Goodman, R. M. Silverstein, and H. Benitez, *J. Am. Chem. Soc.*, **79**, 3073 (1957).

[5] M. F. Shostakovskii, B. A. Sokolov, A. N. Grishko, K. F. Lavrova, and G. I. Kagan, *J. Gen. Chem. USSR*, **32**, 3882 (1962); *Chem. Abstr.*, **58**, 1259 (1963).

[6] J. C. Saam and J. L. Speier, *J. Am. Chem. Soc.*, **83**, 1351 (1961).

[7] T. G. Selin and R. West, *ibid.*, **84**, 1863 (1962).

[8] A. D. Petrov, E. A. Chernyshev, M. E. Dolgaya, Yu. P. Egorov, and L. A. Leites, *J. Gen. Chem. USSR*, **30**, 376 (1960).

[9] R. A. Pike and R. C. Borchert, U. S. Patent 2,954,390 (Sept. 27, 1960).

[10] W. D. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960).

TABLE I

ADDITION OF SILICON HYDRIDES TO ALKENYLBENZENES

$$\underset{(n\ =\ 0,\ 1,\ \text{and}\ 2)}{\equiv\text{SiH} + \text{Ph(CH}_2)_n\text{CH=CH}_2} \xrightarrow[100^\circ]{\text{H}_2\text{PtCl}_6} \underset{\text{A}}{\equiv\text{Si(CH}_2)_{n+2}\text{Ph}} + \underset{\text{C}}{\equiv\text{SiCH(Ph)(CH}_2)_n\text{CH}_3}$$

Olefin/hydride[a]	Ratio[b] of A/C With Me_2ClSiH	With $MeCl_2SiH$	With Cl_3SiH
With $PhCH{=}CH_2$			
36		65/35	
1.8	84/16	61/39	63/37
1.0	85/15, 86/14[c]	69/31, 81/19[c]	57/43, 100/0[c]
0.45	86/14	67/33	57/43
0.23		61/39	
With $PhCH_2CH{=}CH_2$			
1.6	100/0	100/0	78/22
0.4	95/5	89/11	67/33
With $PhCH_2CH_2CH{=}CH_2$			
1.4	100/0	100/0	82/18
0.35	98/2	91/9	70/30

[a] Molar ratio of reagents. [b] Area ratio by vapor phase chromatography (v.p.c.). [c] Tetrahydrofuran was added: 2 v./v. of olefin.

sodium on alumina is a very effective catalyst for the isomerization of olefins to form thermodynamic mixtures of isomers. Excess pentene-1 or -2 was also recoverable from such a reaction as a mixture of isomers. A mixture of pentenes is more easily analyzed than a mixture of phenylalkenes. Therefore, the isomers resulting from the pentenes were examined carefully. See Table II.

TABLE II

ISOMERIZATION OF PENTENES

Source	V.p.c. area, % Pentene-1	*trans*-2	*cis*-2
Pentene-1 + Cl_3SiH/H_2PtCl_6	6	64	30
cis-Pentene-2 + Cl_3SiH/H_2PtCl_6	5	68	27
Pentenes + *t*-$BuOK/Me_2SO$[a]	3.1	60.2	36.9
Pentene-1 + Na/Al_2O_3	1	78	21

[a] Mole % determined by S. Bank, C. A. Rowe, and A. Schriesheim [*J. Am. Chem. Soc.*, **85**, 2115 (1963)] and thought to be at thermodynamic equilibrium.

TABLE III

ADDITION OF SILICON HYDRIDES TO 1-PHENYLALKENES

$$\equiv\text{SiH} + \text{PhCH=CH(CH}_2)_n\text{H} \xrightarrow[100^\circ]{\text{H}_2\text{PtCl}_6} \underset{\text{A}}{\equiv\text{Si(CH}_2)_{n+2}\text{Ph}} + \underset{\text{C}}{\equiv\text{SiCHPh(CH}_2)_n\text{CH}_3}$$

$(n = 0, 1, 2, \text{and } 4)$

Olefin	Silane	Mole ratio, $\frac{\text{olefin}}{\text{silane}}$	V.p.c. area ratio, $\frac{\text{series A}}{\text{series C}}$	Hours at 100°
$PhCH{=}CH_2$	Me_2ClSiH	1.8	84/16	16
	$MeCl_2SiH$	1.8	61/39	16
	Cl_3SiH	1.8	63/47	16
$PhCH{=}CHCH_3$	$MeCl_2SiH$	0.80	49/51	1
$PhCH{=}CHCH_2CH_3$	Me_2ClSiH	1.5	43/57	2
	$MeCl_2SiH$	1.4	39/61	2
	Cl_3SiH	1.4	23/77	2
$PhCH{=}CH(CH_2)_3CH_3$	Me_2ClSiH	1.0	37/63	66
	$MeCl_2SiH$	1.0	32/68	21
	Cl_3SiH	1.0	10/90	24

From these data we conclude that the isomerization of olefins during the addition reactions is probably not stereoselective but tends toward reaching a thermodynamically determined distribution of isomers.

In order to see if the 1-phenylalkenes might be intermediates for the formation of series C from $Ph(CH_2)_n$-$CH{=}CH_2$, the experiments were repeated with 1-phenylalkenes. The results of these experiments are found in Table III.

Nearly quantitative yields of the same series of adducts A and C as shown in Table I were again obtained, but the ratios of A/C were much smaller. These data agree with an assumption that series C results from addition to 1-phenylalkenes, and that the 1-phenylalkenes are intermediates for the (1-phenylalkyl)silanes even when a compound such as 4-phenylbutene-1 is used as the original reagent.

Further to check into this assumption, the rate of disappearance of trichlorosilane and 4-phenylbutene-1, from an equimolar solution of these reagents, and the rate of appearance of products and 1-phenylbutene were determined. The data are summarized in Fig. 1. Note how quickly (4-phenylbutyl)trichlorosilane formed. About 82% of the maximum amount formed within 5 min., during which time 1-phenylbutene appeared along with only 28% of the final amount of the (1-phenylbutyl)silane. The 1-phenylbutene slowly formed chiefly the 1-phenylbutyl adduct. Figure 1 indicates that the 1-phenylalkenes are precursors for the (1-phenylalkyl)silanes.

Tables I and III both show that the ratio of adducts (A/C) is determined in part by the structure of the silicon hydride. The effect of the structure of the silicon hydride was investigated further by determining the ratio of the two isomeric adducts made from styrene with hydrides of the formulas $F_x SiHMe_{3-x}$ and $(Me_3SiO)_x SiHMe_{3-x}$ with $x = 0, 1, 2,$ and 3. The results of these experiments are shown in Fig. 2.

Experiments were also performed to see if substituents on the benzene ring influence the ratio of type A to type C adducts. They do indeed, as shown in Table IV.

The H^1 n.m.r. spectra of compounds of the formula $R'_3SiCH(Ph)R$ (R' = Me or Cl; R = H, Me, Et, *n*-Pr, and *n*-Bu) have been examined. This examination showed a well-resolved doublet for the phenyl proton absorption with a splitting constant of 2–3 c.p.s. (see Table V), except in the spectra of (1-phenylhexyl)-trichlorosilane and (1-phenylethyl)methyldichlorosilane,

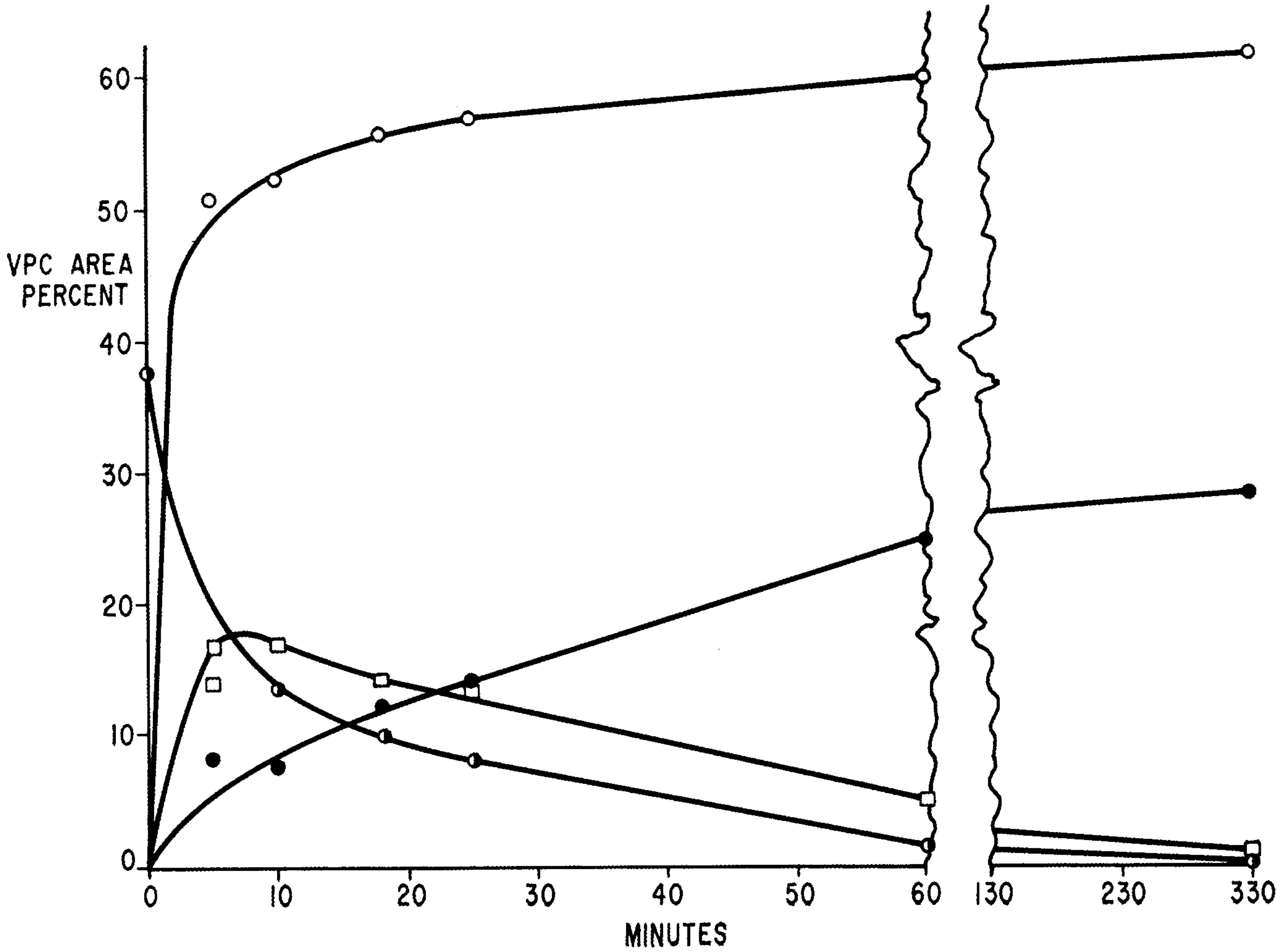

Fig. 1.—Products from the reaction of $PhCH_2CH_2CH{=}CH_2$ and Cl_3SiH at 100° with H_2PtCl_6 as catalyst: ○, $Ph(CH_2)_4SiCl_3$; ●($Cl_3SiCHPh(CH_2)_2CH_3$; □, *trans*-$PhCH{=}CHCH_2CH_3$; ◑, Cl_3SiH.

Table IV

Addition of Silicon Hydrides to Substituted Styrenes

$$\equiv SiH + RCH{=}CH_2 \xrightarrow[100°]{H_2PtCl_6} \underset{A}{\equiv Si(CH_2)_2R} + \underset{C}{\equiv SiCHRMe}$$

R	V.p.c. area ratio of A/C	
	With Cl_3SiH	With $MeCl_2SiH$
C_6H_5–	57/43	69/31
2-ClC_6H_4–	96/4	
4-ClC_6H_4–	68/32	
4-BrC_6H_4–	68/32	72/28
F_5C_6–	100/0	100/0
2,4,5-$Cl_3C_6H_2$–	100/0	100/0
2,6-$Me_2C_6H_3$–	100/0	100/0
4-MeC_6H_4–	100/0	64/36

which showed only a singlet for the phenyl protons. The H^1 n.m.r. spectra of several (phenylalkyl)trimethylsilanes and one (phenylalkyl)methyldichlorosilane not having the silicon α to the phenyl group showed no such phenyl proton splitting.

It is our belief that the splitting of phenyl protons in (1-phenylalkyl)trimethylsilanes is sufficiently characteristic of the $Me_3SiCHPh$– group to be of diagnostic value.

Discussion

The isomerization of the alkenylbenzenes in this work is in agreement with previous observations explained recently in a qualitative way by Ryan and Speier.[11]

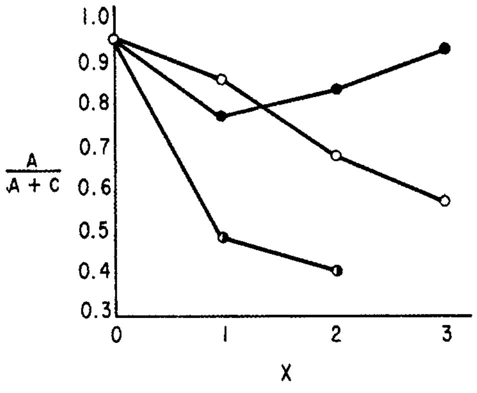

Fig. 2.—$Y_xMe_{3-x}SiH$ + $PhCH{=}CH_2$ → $Y_xMe_{3-x}SiCH_2CH_2Ph$ + $Y_xMe_{3-x}SiCHMePh$: ● = Y is $OSiMe_3$, ○ = Y is Cl, ◑ = Y is F; *A* and *C* are v.p.c. areas in this ratio.

None of these new data is contrary to the postulates of the mechanism previously suggested,[11] but that mechanism is not yet adequate to explain the formation of only two adducts from a compound like 4-phenylbutene-1. It offers no suggestions as to how substituents on the silicon hydride or in the substituted styrenes should influence the ratio of adducts made in any case.

Much thought on these data convinces us that more is required before a satisfactory explanation is possible.

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[11] J. W. Ryan and J. L. Speier, *J. Am. Chem. Soc.*, **86**, 895 (1964).

TABLE V

H^1 N.M.R. ABSORPTIONS OF SEVERAL (PHENYLALKYL)SILANES

Compound	H^1 n.m.r. absorptions[a]
Me_3SiCH_2Ph[b]	3.57 d[c] (2.4),[d] 8.57 s, 10.30 s
$Me_3Si(CH_2)_2Ph$[e]	2.93 s, 7.43 q, 9.20 q, 10.03 s
$MeF_2Si(CH_2)_2Ph$	2.85 s, 7.28 q, 8.90 se, 9.85 t
$Me_3Si(CH_2)_3Ph$	2.94 s, 7.43 t, 8.39 q, 9.52 c, 10.03 s
$MeCl_2Si(CH_2)_3Ph$	2.93 s, 7.49 t, 8.29 q, 9.08 t, 9.49 s
$Me_3SiCH_2CHPhCH_3$[e]	2.92 s, 7.16 se, 8.76 d, 9.10 d, 10.13 s
$Me_3Si(CH_2)_4Ph$	2.95 s, 7.47 t, 8.50 c, 9.50 t, 10.03 s
$Cl_3Si(CH_2)_6Ph$	2.92 s, 7.44 t, 8.34 c, 8.60 s
$MeF_2SiCHPhCH_3$	2.89 s, 7.71 qu, 8.58 d, 9.90 t
$Me_3SiCHPhCH_3$	2.98 d (2.4), 7.91 qu, 8.68 d, 10.08 s
$MeCl_2SiCHPhCH_3$[e]	2.70 s, 7.54 qu, 8.50 d, 9.46 s
$Me_3SiCHPhCH_2CH_3$	2.98 d (2.4), 8.24 c, 9.14 t, 10.08 s
$Me_3SiCHPh(CH_2)_2CH_3$	2.98 d (2.0), 8.12 c, 8.25–9.00 c, 9.13 c, 10.07 s
$Me_3SiCHPh(CH_2)_4CH_3$	3.00 d (3.0), 8.17 c, 8.78 c, 9.17 c, 10.05 s
$Cl_3SiCHPh(CH_2)_4CH_3$	2.83 s, 7.26 d, 7.42 d, 7.97 c, 8.75 c, 9.17 c

[a] All absorptions are in units of τ relative to tetramethylsilane (internal). [b] This compound was donated by W. A. Finzel, b.p. 97° (40 mm.), n^{25}_{D} 1.4912. [c] Letters following the frequencies refer to first-order splitting: s, singlet; d, doublet; t, triplet; qu, quartet; q, quintet; se, sextet; and c, complex absorption. [d] Splitting constants are reported in cycles per second. [e] This compound was donated by J. W. Ryan.[3]

Experimental

Instrumental Analyses.—Vapor phase chromatographic analyses (v.p.c.) were performed either on a 4- or a 10-ft. 1/4-in. stainless steel column packed with 23% by weight Dow Corning 200 gum on Chromosorb W. Peak areas were calculated from the product of the peak height and the width of the peak at one-half the height. Nuclear magnetic resonance proton spectra (H^1 n.m.r.) were obtained on a Varian Associates Model A-60 spectrometer operating at a radio frequency of 60 Mc/sec. using pure liquids with 1% tetramethylsilane as the internal standard.

Preparation of Starting Materials.—4-Phenylbutene-1 was prepared in 66% yield by coupling benzylmagnesium chloride with allyl chloride; b.p. 180–181° at 747 mm., n^{25}_{D} 1.5051, d^{25}_{4} 0.8775; lit.[12] b.p. 181.1° at 760 mm., n^{20}_{D} 1.50748, d^{20}_{4} 0.88153. *trans*-1-Phenylpropene was obtained as a by-product from the free-radical chlorination of *n*-propylbenzene by sulfuryl chloride; b.p. 72° at 20 mm., n^{25}_{D} 1.5473; lit.[13] for *trans* b.p. 73.5° at 20 mm., n^{25}_{D} 1.5473; lit.[13] for *cis* b.p. 64.5° at 20 mm., n^{25}_{D} 1.5400. V.p.c. indicated this compound to be pure and its infrared spectrum showed the strong absorption at 10.4 μ for a *trans*-ethylenic double bond. *trans*-1-Phenylhexene (b.p. 130° at 29 mm., n^{25}_{D} 1.5263, d^{25}_{4} 0.8809; lit.[14] b.p. 108.5-109° at 10 mm., n^{30}_{D} 1.52327, d^{30}_{4} 0.87923) was preparedin 49 % yield from the dehydration of 1-phenylhexanol (b.p. 84–86° at 0.3 mm., n^{25}_{D} 1.5026, d^{25}_{4} 0.9453; lit.[15] b.p. 131-134° at 11 mm.[15]) over Al_2O_3 at 425°. V.p.c. indicated the compound to be pure and its infrared spectrum showed the strong absorption at 10.4 μ for a *trans*-ethylenic double bond. In addition to the *trans* olefin a 34% yield of isomeric phenylhexenes was obtained, b.p. 94–99° at 10 mm.

Methyldifluorosilane was prepared in 75% yield from boron trifluoride etherate (180 g., 1.33 moles) in ether and methylhydrogenpolysiloxane $(MeHSiO)_x$ (60 g.).

Boron trifluoride (65 g., 0.5 mole) was passed into dry *n*-butyl ether and then *sym*-tetramethyldisiloxane (62 g., 0.5 mole) was added slowly. Essentially pure dimethylfluorosilane (72% yield) boiled from the solution into a cold trap.

These products were slowly evaporated from one trap into another and characterized by their H^1 n.m.r. spectra. The spectrum of methyldifluorosilane consisted of a triplet at τ 0.31, 0.42, and 0.53 for the methyl protons with each peak split into a doublet (coupling constant = 1.2 c.p.s.). The silane hydrogen appeared as a triplet at τ 3.69, 4.82, and 5.95 with each peak split into a quartet (coupling constant = 1.1 c.p.s.). The spectrum of dimethylfluorosilane consisted of a pair of doublets at τ 0.24 and 0.36 (coupling constant = 2.7 c.p.s.) for the methyl protons. The silane hydrogen appeared as a pair of septets at τ 4.42 and 5.29 (coupling constant = 2.7 c.p.s.).

Pentamethyldisiloxane used in these experiments was redistilled, b.p. 85° at 750 mm., n^{25}_{D} 1.3715, d^{25}_{4} 0.7546, R_{D} 0.3008 (calcd. R_{D} 0.3000).

Bistrimethylsiloxymethylsilane was prepared in a 55% yield by the acid-catalyzed equilibration of hexamethyldisiloxane (275 g., 16.9 moles) with 2,4,6,8,10-pentamethylcyclopentasiloxane (359 g., 5.97 moles); b.p. 66° at 59 mm., n^{25}_{D} 1.3800, d^{25}_{4} 0.8136, R_{D} 0.2847 (calcd. R_{D} 0.2841); lit.[16] b.p. 142° at 760 mm., n^{20}_{D} 1.3818, d^{20}_{4} 0.8194.

Anal. Calcd. for $C_7H_{22}O_2Si_3$: Si, 37.85; SiH, 0.449. Found: Si, 37.95; SiH, 0.453.

Tristrimethylsiloxysilane was prepared in an 8% yield by the cohydrolysis of trichlorosilane and trimethylchlorosilane in isopropyl alcohol solvent; b.p. 84–87° at 30 mm., n^{25}_{D} 1.3846, d^{25}_{4} 0.846, R_{D} 0.2767 (calcd. R_{D} 0.2777); lit.[17] b.p. 67–68° at 11 mm., n^{20}_{D} 1.3860, d^{20}_{4} 0.854.

Anal. Calcd. for $C_9H_{28}O_3Si_4$: Si, 37.88; SiH, 0.340. Found: Si, 37.8; SiH, 0.326.

Other Materials Used.—Trichlorosilane, methyldichlorosilane, and dimethylchlorosilane were redistilled production grade chemicals from the Dow Corning Corp. Allylbenzene was obtained from Matheson Coleman and Bell Corp., n^{25}_{D} 1.5107. Pentene-1 and *cis*-pentene-2 were technical grade chemicals (95% minimum) from Phillips Petroleum Co. Styrene was production grade from The Dow Chemical Co. The catalyst used was in the form of a 0.1 *M* solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol.

Addition of Methyldichlorosilane to *trans*-1-Phenylpropene.—*trans*-1-Phenylpropene (28.7 g., 0.243 mole), methyldichlorosilane (28.0 g., 0.243 mole), and 0.024 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol were heated at reflux for 18 hr. V.p.c. showed that the reaction was then essentially complete and that (1-phenyl- and 3-phenylpropyl)methyldichlorosilanes were made with a v.p.c. area ratio of 32:68. No trace of (2-phenylpropyl)methyldichlorosilane was detected.

The mixture was treated with excess methylmagnesium bromide in ether in the usual manner and carefully distilled to give (1-phenylpropyl)trimethylsilane (24% yield over-all with a purity of 98%), b.p. 112° at 35 mm., n^{25}_{D} 1.4927, d^{25}_{4} 0.8680, R_{D} 0.3348 (calcd. R_{D} 0.3323).

Anal. Calcd. for $C_{12}H_{20}Si$: Si, 14.59. Found: 14.73.

This compound was heated with alcoholic alkali to form *n*-propylbenzene.

The H^1 n.m.r. spectrum was typically that of an α-alkylbenzylsilane showing no benzyl proton absorption, a phenyl proton doublet, and a methyl proton absorption split into a triplet by adjacent methylene protons. The (3-phenylpropyl)trimethylsilane was also isolated (20% yield of 99.5% purity); b.p. 119° at 36 mm., n^{25}_{D} 1.4839, d^{25}_{4} 0.8590, R_{D} 0.3300 (calcd. R_{D} 0.3323); lit.[18] b.p. 78° at 6.5 mm., n^{20}_{D} 1.4865, d^{20}_{4} 0.8664; lit.[8] b.p. 56° at 2 mm., n^{20}_{D} 1.4853, d^{20}_{4} 0.8684.

Anal. Calcd. for $C_{12}H_{20}Si$: Si, 14.59. Found: 14.89.

The H^1 n.m.r. spectrum of this compound showed the typical chemical shifts for the starred protons of $(CH_3)_3SiCH_2^*$–, $-CH_2-CH_2^*-CH_2-$, and $C_6H_5CH_2^*$–. This compound was not affected by hot alcoholic alkali.

Addition of Methyldichlorosilane to Allylbenzene.—Allylbenzene (35.4 g., 0.300 mole), methyldichlorosilane (34.5 g., 0.300 mole), and 0.029 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol were treated as above. A rapid exothermic reaction occurred which was apparently complete within 5 min. V.p.c. analysis showed the same two adducts that were formed from 1-phenylpropene in the ratio of 6/94. The mixture was carefully distilled. The lower boiling (1-phenylpropyl)methyldichlorosilane was present in too small an amount to be separated as a pure fraction, but the higher boiling (3-phenylpropyl)-

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methyldichlorosilane was isolated in 70% yield with a purity above 97%; b.p. 143° at 20 mm., $n^{25}\mathrm{D}$ 1.5090, d^{25}_{4} 1.1020, R_{D} 0.2691 (calcd. R_{D} 0.2709); lit.[8] b.p. 114° at 6 mm., $n^{20}\mathrm{D}$ 1.5105, d^{20}_{4} 1.1093.

Anal. Calcd. for $C_9H_{11}CH_3SiCl_2$: neut. equiv., 116.6. Found: neut. equiv., 117.0.

Addition of Trichlorosilane to Allylbenzene.—Allylbenzene (23.3 g., 0.197 mole), trichlorosilane (33.9 g., 0.250 mole), and 0.021 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol were heated at reflux for 5 hr. V.p.c. analysis then showed that the reaction was complete and that again two products were made with an area ratio of 14:86, nonterminal to terminal adduct. The mixture was treated with excess methylmagnesium bromide. The products were separated and identified by v.p.c. as being (1-phenylpropyl)trimethylsilane and (3-phenylpropyl)trimethylsilane with an area ratio of 13:87. The identification of these compounds was by comparison of their retention times with previously identified samples and by treatment with hot alcoholic caustic. A sample of the mixture treated with hot alcoholic alkali formed *n*-propylbenzene and unchanged (3-phenylpropyl)-trimethylsilane in a ratio of 13:87 measured as v.p.c. areas.

Addition of Trichlorosilane to 4-Phenylbutene-1.—Trichlorosilane (226 g., 1.67 moles) was added slowly to 4-phenylbutene-1 (200 g., 1.51 moles) which contained 0.23 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol at 100° and refluxed for 3 hr. V.p.c. analysis showed two adducts, with an area ratio of 21:79, nonterminal to terminal adduct. The solution was methylated with excess methylmagnesium bromide and distilled after normal work-up to give (1-phenylbutyl)trimethylsilane (12% over-all yield of 99.5% purity), b.p. 129° at 30 mm., $n^{25}\mathrm{D}$ 1.4917, d^{25}_{4} 0.8661, R_{D} 0.3348 (calcd. R_{D} 0.3323).

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.61. Found: Si, 13.6.

The H^1 n.m.r. spectrum of this compound did not conclusively identify the structure. It did, however, have the normal absorptions for $C_6H_5{}^*$–, –C–$CH_3{}^*$, and $(CH_3{}^*)_3Si$– at τ-values of 2.98, 9.00,[19] and 10.07, respectively, and contained no absorption at 7.38 typical of $C_6H_5CH_2{}^*$–.[19] The cleavage of this sample by alcoholic alkali is described in the last section of this paper. The (4-phenylbutyl)trimethylsilane was also isolated (29% over-all yield of 99.5% purity); b.p. 146° at 30 mm., $n^{25}\mathrm{D}$ 1.4820, d^{25}_{4} 0.8558, R_{D} 0.3331 (calcd. R_{D} 0.3323).

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.61. Found: Si, 13.4.

This isomer was unchanged by hot alcoholic alkali.

The H^1 n.m.r. spectrum of this compound had the typical chemical shifts for the benzyl and silylmethylene protons in addition to the rather broad symmetrical absorptions of the nearly equivalent β- and γ-methylene protons. The physical properties[8] are b.p. 91–92° at 3 mm., $n^{20}\mathrm{D}$ 1.4835, d^{20}_{4} 0.8653. Along with these two adducts *trans*-1-phenylbutene was recovered in a 5.8% yield with a v.p.c. purity of greater than 95%; b.p. 102° at 30 mm., $n^{25}\mathrm{D}$, 1.5386, d^{25}_{4} 0.9011; lit.[20] b.p. 197.4° at 738 mm., $n^{20}\mathrm{D}$ 1.5420, d^{25}_{4} 0.90186. The infrared spectrum of this compound had the strong absorption at 10.4 μ for a *trans*-ethylenic double bond and v.p.c. indicated only one compound. For comparison, the physical properties of *cis*-1-phenylbutene[20] are b.p. 185.6° at 737 mm., $n^{20}\mathrm{D}$ 1.5284, d^{20}_{4} 0.89772, and of 1-phenylbutene-2[21] are 48.5° at 4 mm., $n^{20}\mathrm{D}$ 1.5115.

Addition of Trichlorosilane to *trans*-1-Phenylhexene.—A solution of trichlorosilane (20.6 g., 0.152 mole), *trans*-1-phenylhexene (23.6 g., 0.147 mole), and 0.03 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol was heated for 18 hr., at which time the temperature was 190°. V.p.c. analysis showed two products, (6-phenylhexyl- and 1-phenylhexyl)trichlorosilane, with an area ratio of 13:87, respectively. Distillation of the crude solution gave a 78% yield of (1-phenylhexyl)trichlorosilane, b.p. 80° at 0.07 mm., $n^{25}\mathrm{D}$ 1.5098, d^{25}_{4} 0.8732, R_{D} 0.2611 (calcd. R_{D} 0.2589).

Anal. Calcd. for $C_{12}H_{17}SiCl_3$: neut. equiv., 98.58. Found: neut. equiv., 98.4.

A 13% yield of 6-phenylhexyltrichlorosilane was also isolated, b.p. 92° at 0.07 mm., $n^{25}\mathrm{D}$ 1.5052.

Anal. Calcd. for $C_{12}H_{17}SiCl_3$: neut. equiv., 98.58. Found: neut. equiv., 99.4.

The H^1 n.m.r. spectrum of (1-phenylhexyl)trichlorosilane shows how an asymmetric center adjacent to a methylene group makes the methylene protons nonequivalent. The result of this nonequivalence was the formation of a pair of doublets at τ 7.26 and 7.42 (splitting constants of 5 c.p.s. each). The integrated peak areas for the aliphatic protons in order of increasing τ were 1.0:2.0:6.0:2.9. The spectrum of the 6-phenylhexyl isomer was quite simple, showing a phenyl proton singlet, a benzyl proton triplet, and a very broad single peak for the other aliphatic protons. The integrated peak areas of 4.9:2.0:9.9, respectively, is consistent with the proposed structure. When these two isomers were treated with hot alcoholic caustic, *n*-hexylbenzene was obtained from the 1-phenylhexyl adduct while only high boiling residue was obtained from the 6-phenylhexyl adduct.

Permethylation of (1-phenylhexyl)trichlorosilane (10.1 g., 0.0342 mole) with excess methylmagnesium bromide in the usual manner gave upon distillation 5.6 g. of (1-phenylhexyl)-trimethylsilane (70% yield); b.p. 70–72° at 0.2 mm., $n^{25}\mathrm{D}$ 1.4889, d^{25}_{4} 0.8631, R_{D} 0.3343 (calcd. R_{D} 0.3322). The H^1 n.m.r. spectrum was consistent with the proposed structure, giving the expected proton ratio and the phenyl proton doublet of an α-trimethylsilylalkylbenzene. The trimethylsilyl group was also cleaved by alkali to give *n*-hexylbenzene.

Addition of Silicon Hydrides to Styrene.—An equimolar solution of styrene and tristrimethylsiloxysilane containing 10^{-4} to 10^{-5} moles of chloroplatinic acid per mole of styrene was heated in a flask. The reaction proceeded smoothly to greater than 90% completion by v.p.c. Similar reactions were carried out with bistrimethylsiloxymethylsilane and pentamethyldisiloxane. The area ratios of isomeric products from each reaction by v.p.c. were 93:7, 84:16, and 79:21, respectively, (2-phenylethyl- to 1-phenylethyl)silane.

Methyldifluorosilane (0.50 mole) was bubbled into styrene (52.1 g., 0.50 mole) containing 0.1 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol at a temperature of 50 to 90°. V.p.c. analysis indicated the reaction to be 58% complete with an area ratio of 37:63 (2-phenylethyl- to 1-phenylethyl)methyldifluorosilane. Distillation yielded the 2-phenylethyl isomer in a 20% yield; b.p. 191° at 746 mm., $n^{25}\mathrm{D}$ 1.4562, d^{25}_{4} 1.058, R_{D} 0.2570 (calcd. R_{D} 0.256); lit.[5] b.p. 184° at 728 mm., $n^{20}\mathrm{D}$ 1.4600, d^{20}_{4} 1.0674.

Anal. Calcd. for $C_9H_{12}F_2Si$: neut. equiv., 93.14; F, 20.40. Found: neut. equiv., 93.9; F, 20.4 (% by n.m.r.).

Also obtained was the 1-phenylethyl isomer in a 14% yield; b.p. 181° at 746 mm., $n^{25}\mathrm{D}$ 1.4602, d^{25}_{4} 1.063, R_{D} 0.2579 (calcd. R_{D} 0.256); lit.[5] b.p. 178° at 728 mm., $n^{20}\mathrm{D}$ 1.4620, d^{20}_{4} 1.0668.

Anal. Calcd. for $C_9H_{12}F_2Si$: neut. equiv., 93.14; F, 20.40. Found: neut. equiv., 94.2; F, 20.4 (% by n.m.r.).

The structures of these isomers were confirmed by their H^1 n.m.r. spectra (see Table IV).

Dimethylfluorosilane (2.3 g., 0.0029 mole), styrene (3.1 g., 0.0029 mole), and 0.01 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol were sealed in a Pyrex tube and heated at 100° for 30 min. V.p.c. analysis indicated the reaction to be greater than 95% complete with two isomeric products being present with an area ratio of 49:51, (2-phenylethyl- to 1-phenylethyl)-dimethylfluorosilane.

Addition of Dimethylfluorosilane to Hexene-2.—Hexene-2 (2.03 g., 0.024 mole), dimethylfluorosilane (1.88 g., 0.024 mole), and 0.005 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol were sealed in a Pyrex tube and heated at 100° for 18 hr. V.p.c. analysis indicated the reaction to be nearly complete with only one product. The product was methylated with methylmagnesium iodide to give 1-hexyltrimethylsilane in a 12% yield; b.p. 65–67° at 30 mm., $n^{25}\mathrm{D}$ 1.4131, d^{25}_{4} 0.7429, R_{D} 0.3357, calcd. R_{D} 0.3375; lit.[22] b.p. 163° at 760 mm., $n^{20}\mathrm{D}$ 1.4154, d^{20}_{4} 0.7422.

Very careful analysis of the permethyl derivative by a capillary column v.p.c. capable of resolving the 1-, 2-, and 3-hexyltrimethylsilanes showed only that 1-hexyltrimethylsilane was present. Its infrared spectrum was identical with that of an authentic sample of 1-hexyltrimethylsilane prepared from the coupling of 1-hexyllithium with trimethylchlorosilane, b.p. 161° at 731 mm., $n^{25}\mathrm{D}$ 1.4142, d^{25}_{4} 0.7474.

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Addition of Trichlorosilane to 4-Phenylbutene-1, Rate Study.—Into each of eight 1 × 20 cm. Pyrex tubes cooled in Dry Ice were sealed 0.01 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol and 2.0 ml. of an equimolar solution of trichlorosilane in 4-phenylbutene-1. The tubes were heated in a boiling water bath, cooled by Dry Ice, and analyzed immediately by v.p.c. The first tube was heated only 5 min., after which it contained little or no 4-phenylbutene-1, but *trans*-1-phenylbutene with a trace of another olefin which has not been identified. The successive tubes, each heated for a longer time, showed that the *trans*-1-phenylbutene and the unidentified olefin slowly disappeared as the relative amount of (1-phenylbutyl)trichlorosilane increased (see Fig. 2).

Addition of Trichlorosilane to *cis*-Pentene-2 and Pentene-1.—In a similar manner pentene-1 and *cis*-pentene-2 (1.00 ml.) were heated for 10 min. in sealed tubes at 100° with trichlorosilane (0.50 ml.) and 0.0025 ml. of 0.1 *M* chloroplatinic acid. Analysis by v.p.c. and infrared showed that all of the trichlorosilane was gone and that *n*-pentyltrichlorosilane was the only adduct. The distribution of isomers in the recovered olefins can be found in Table II.

Isomerization of 4-Phenylbutene-1.—4-Phenylbutene-1 (10 ml.) and 3.9 g. of 8% sodium on alumina were heated at 58° in a dry 20-ml. ampoule for 48 hr. The isomerization proceeded smoothly but slowly. V.p.c. analysis showed the presence of four olefins, two of which were 4-phenyl- and *trans*-1-phenylbutene. Ninety-one per cent of the total area was due to *trans*-1-phenylbutene. A 0.05-ml. sample of the mixture was chromatogrammed and the major compound collected to give a pure fraction having the infrared spectrum of a *trans* olefin and a refractive index of n^{25}_{D} 1.5395.

Cleavage of (1-Phenylbutyl)trimethylsilane with Alcoholic Caustic.—All (phenylalkyl)silanes in this study were treated with alcoholic caustic to determine those compounds containing a silicon attached to a position α to a benzene ring.[23] (1-Phenylbutyl)trimethylsilane (15.4 g.), potassium hydroxide (34.2 g.), absolute ethanol (51 ml.), and water (3 ml.) were heated at reflux (108°) for 22 hr. The organic layer was separated, washed with water, dried with anhydrous sodium sulfate, and carefully distilled to give a 95% yield of *n*-butylbenzene, b.p. 185° at 746 mm., n^{25}_{D} 1.4872, d^{25}_{4} 0.8548. V.p.c. analysis before distillation showed that all of the (1-phenylbutyl)trimethylsilane had been cleaved. The infrared spectrum and v.p.c. retention time of this product were identical with those of an authentic sample of *n*-butylbenzene prepared by the reaction of *n*-butylbromide, bromobenzene, and sodium; b.p. 185° at 740 mm., n^{25}_{D} 1.4873, d^{25}_{4} 0.8585; lit.[12] b.p. 182.9° at 760 mm., n^{20}_{D} 1.48975, d^{20}_{4} 0.86017.

The other samples mentioned in this paper were subjected to treatment with alcoholic caustic as here described, but the products were identified only by their v.p.c. retention times.

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The Free-Radical Addition of Deuterium Bromide to *cis*- and *trans*-1-Deuterio-1-hexene[1]

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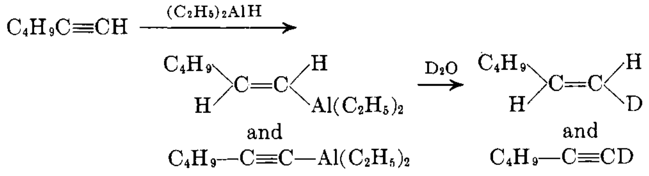
Received April 2, 1964

The radical-chain addition of deuterium bromide to a terminal olefin, 1-deuterio-1-hexene, is a stereospecific reaction.

The stereochemistry of free-radical additions of hydrogen bromide and deuterium bromide to olefins has aroused considerable interest. The interest in this topic has been generated by studies which have demonstrated that hydrogen bromide adds in a completely *trans* manner to 1-methylcyclohexene,[3] 1-bromocyclohexene,[4] and 1-chlorocyclohexene.[4] However, in the similar 1-bromocyclobutene, 1-bromocyclopentene, and 1-bromocycloheptene systems, even though a preference remains for *trans* addition, the reactions are no longer completely stereospecific.[5] In a somewhat more complex, but still similar system, 2-bromo-2-norbornene, reaction with hydrogen bromide gives predominantly *cis* addition.[6]

In acyclic systems radical additions of deuterium bromide to *cis*- and *trans*-2-butenes[7] are stereospecific and *trans*, and hydrogen bromide additions to 2-bromo-2-butenes are 90–95% *trans* additions, the source of the contaminating isomers being undetermined.[8]

Since all previous studies had been constrained to nonterminal olefins, the stereochemistry of additions to terminal olefins was investigated using 1-deuterio-1-hexene and deuterium bromide. The procedure of Wilke and Müller[9] for the synthesis of *trans*-1-deuterio-1-hexene was used with somewhat different results. Whereas Wilke and Müller found that the addition of diethylaluminum hydride to 1-hexyne, followed by deuterolysis, yields *trans*-1-deuterio-1-hexene, in our hands the reaction gave varying ratios of *trans*-1-deuterio-1-hexene and 1-deuterio-1-hexyne, which were dependent on the reaction temperature. Addition of diethylaluminum hydride to 1-hexyne at 35–45° gave a 44% yield of *trans*-1-deuterio-1-hexene and a 12% yield of 1-deuterio-1-hexyne. When the reaction was carried out at a lower temperature (5–15°), a 76% yield of *trans*-1-deuterio-1-hexene and 10% yield of 1-deuterio-1-hexyne was obtained. The 1-deuterio-1-hexyne was removed by shaking the product with aqueous ammoniacal silver nitrate solution.



The infrared spectrum[10] of the purified product was identical with that prepared by Wilke and Müller.[9] Although comparison with the spectrum of *cis*-1-deuterio-1-hexene failed to indicate the presence of this

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[1] This was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-457.

[2] The Pennsylvania State University, 1958–1959.

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