Journal of Organometallic Chemistry, 156 (1978) 235—244
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CHLOROPLATINIC ACID CATALYZED ADDITIONS OF SILANES TO ISOPRENE *

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(Received February 27th, 1978)

Summary

The chloroplatinic acid catalyzed hydrosilylation of isoprene with trichloro-, dichloromethyl-, and trimethylsilane has been reinvestigated with the purpose of establishing the mode of addition to the substrate. This was accomplished by identifying the structures of the 1/1 adducts, their methylated derivatives and the saturated analogs of the latter. Trichlorosilane added 1,4 to the less hindered side of isoprene; dichloromethylsilane added both 1,2 and 1,4 to the less hindered side and trimethylsilane added 1,2 and 1,4 to both sides of isoprene. These results are contrary to those previously reported in the literature.

Introduction

Several examples of the use of isoprene as a substrate in hydrosilylation reactions have appeared in the literature [1—9]. Since isoprene is an unsymmetrical conjugated diene, addition is possible from either the less or more hindered side. Based on published results, the mode of addition seemingly depends upon the nature of the silane and the catalyst system employed. An example of 1,2-addition to the less hindered side has been reported [1,2], but 1,4-addition appears to be preferred. Additions of the 1,4-variety to both sides of the molecule have been reported with dichloromethylsilane (nickel phosphine catalysis [3]) and with trimethylsilane (chromium hexacarbonyl catalyzed photolysis [4]). Predominantly 1,4-addition to the more hindered size has been reported in a number of systems: trichlorosilane catalyzed by palladium—phosphine systems [5] or bis(benzonitrile)dichloropalladium (II) [6] and trialkoxy-

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* This paper is dedicated to Professor Herbert C. Brown for his many contributions to Chemistry.

** Abstracted in part from the thesis submitted by F.M.M. in partial fulfillment of the requirements for the Ph.D. degree, Purdue University, May 1976.

*** Abstracted in part from the thesis submitted by R.T.R. in partial fulfillment of the requirements for the Ph.D. degree, Purdue University, Dec. 1974.

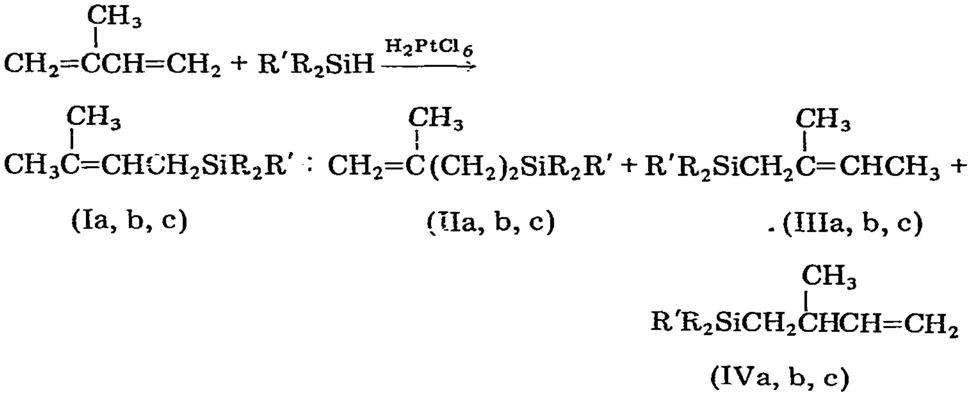
and triethyl-silanes catalyzed by Ziegler systems [7]. A series of silanes was reported by Post [8] and Mamedaliev [9] to add exclusively 1,4 to the more hindered side of isoprene when catalyzed by chloroplatinic acid.

In view of the general randomness of addition observed for most of these reactions, the high specificity claimed by Post [8] and Mamedaliev [9] seemed particularly unexpected. Accordingly, the addition to isoprene of three selected members of the series of silanes reported by these authors (trichlorosilane, dichloromethylsilane, and trimethylsilane) were chosen for reinvestigation. The objective was to determine whether the reaction was indeed as selective in the presence of chloroplatinic acid as reported.

Results and discussion

Possible 1/1 adducts from hydrosilylation of isoprene are shown in Scheme 1.

SCHEME 1



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}CH{=}CH_2 + R'R_2SiH \xrightarrow{H_2PtCl_6}$$

$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2SiR_2R' : CH_2{=}\overset{CH_3}{\overset{|}{C}}(CH_2)_2SiR_2R' + R'R_2SiCH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 +$$

(Ia, b, c) (IIa, b, c) (IIIa, b, c)

$$R'R_2SiCH_2\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2$$

(IVa, b, c)

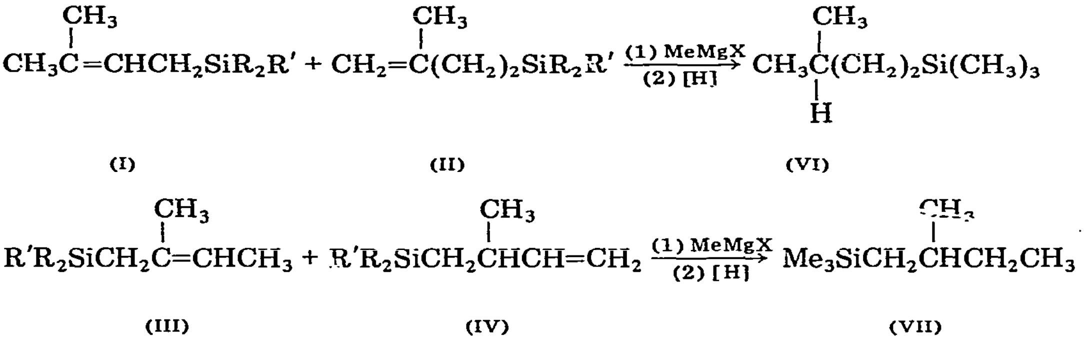
(a: $R = Cl, R' = CH_3$; b: $R = R' = CH_3$; c: $R = R' = Cl$)

Products of type I and II would be formed by 1,4- or 1,2-addition to the less hindered side of isoprene. Products of type III and IV would be formed by a 1,4- of 1,2-addition to the more hindered side. The 1/1 adducts found in this investigation were of types I, II and III only.

The vinyl region of the proton NMR spectrum provided a diagnostic tool for differentiating among compounds I, II and III. Compounds of type I give a vinyl region triplet, while compounds of type III give a quartet. Both signals exhibit secondary splitting and integrate for one proton. These patterns have been reported [4] for structures I and III where $R = R' = CH_3$. Compounds of type II give a tight vinyl multiplet integrating for two protons [10].

Methylation of the 1/1 olefinic adducts followed by reduction [11] to the saturated hydrocarbons, gave a diagnostic tool for determining which side of the isoprene was attacked. As depicted in Scheme 2 below, the less hindered side addition products I and II would result in the formation of 1-trimethylsilyl-3-methylbutane (VI), while the more hindered side addition products III or IV would produce 1-trimethylsilyl-2-methylbutane (VII).

SCHEME 2



$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2SiR_2R' + CH_2=\overset{CH_3}{\overset{|}{C}}(CH_2)_2SiR_2R' \xrightarrow[(2)\,[H]]{(1)\,MeMgX} CH_3\underset{\underset{H}{|}}{\overset{CH_3}{\overset{|}{C}}}(CH_2)_2Si(CH_3)_3$$

(I) (II) (VI)

$$R'R_2SiCH_2\overset{CH_3}{\overset{|}{C}}=CHCH_3 + R'R_2SiCH_2\overset{CH_3}{\overset{|}{C}}HCH=CH_2 \xrightarrow[(2)\,[H]]{(1)\,MeMgX} Me_3SiCH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$$

(III) (IV) (VII)

Typical results of the addition reactions are listed in Table 1.

The major mode of addition of trichlorosilane to isoprene was to the less hindered side via the 1,4-route. No evidence for the formation of *Z*- and *E*-1-trichlorosilyl-2-methyl-2-butene (IIIc) from addition to the more hindered side was observed, contrary to published [8,9] results. When the exact conditions [8] of Post were employed (Table 1, entry 1), 1-trichlorosilyl-3-methyl-2-butene (Ic, 72%), and small amounts of 4-trichlorosilyl-2-methyl-1-butene (IIc) and 1,4-bis(trichlorosilyl)-2-methylbutane (Vc) were the only products obtained. Treatment of the 1/1 adducts according to Scheme 2 led to the isolation of 1-trimethylsilyl-3-methylbutane (VI) in 49% yield.

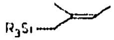
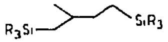
Under milder conditions, the addition reaction proceeded with essentially the same results. For example, at 100°C for 0.5 h in a stainless steel vessel rather than a Carius tube, with a four-fold excess of trichlorosilane (Table 1, entry 2) only (Ic, 67%) and (Vc, 12%) were obtained. If any IIc had formed, it was probably converted to Vc. The terminal vinylidene group would readily add a second equivalent of trichlorosilane since the latter was present in large excess.

Additions of dichloromethylsilane were not as selective as those of trichlorosilane but still resulted in attack from the less hindered side as the major reaction pathway. Employing Post's conditions [8] (Carius tube, 165°C, 17 h, 20% excess of silane) resulted in 1-dichloromethylsilyl-3-methyl-2-butene (Ia, 51%) and 4-dichloromethylsilyl-2-methyl-1-butene (IIa, 3%) as the only observable 1/1 adducts. These products were not cleanly separable by distillation or VPC but the relative amounts were obtainable by integration of the vinyl resonances in the NMR. Compound Ia showed the expected triplet at δ 5.24 and IIa showed a tight multiplet at δ 4.84 ppm. The only other product was 1,4-bis(dichloromethylsilyl)-2-methylbutane (25%).

By altering the stoichiometry to a 25% excess of isoprene, the addition of dichloromethylsilane was found to be complete at 165°C within 0.5 h. The following yields were obtained under these conditions: 53—58% (Ia) with possibly as much as 16% attributable to IIIa, 31—39% IIa, and 6—9% of the 1,4-bis-product. An excess of isoprene increased dramatically the yield of the 1,2 less hindered side adduct (IIa) at the expense of the bis adduct, while the yield of Ia only varied by 6—7%. This suggested that most of the bis adduct was formed by addition of a second equivalent of silane to the terminal vinylidene of IIa instead of to the crowded internal olefin Ia. The possible presence of compound

TABLE 1

CHLOROPLATINIC ACID[a] CATALYZED ADDITIONS OF SILANES TO ISOPRENE

Silane	Stoichiometry[c]	T (°C)	Time (h)	Products (% Yield)[b]			
				 (I a,b,c)	 (II a,b,c)	 Z- and E- (III a,b,c)	 (V)
1 HSiCl$_3$	1	165	17	72	d	0	6
2 [e]	0.25	100	0.5	67	—	0	12
3 HSiCl$_2$Me	0.83	165	17	51	3	0	25
4 HSiCl$_2$Me	1.25	165	17	57	31	f	9
5 HSiCl$_2$Me	1.25	165	0.5	58	34	f	6
6 [e,g]	1.25	165	0.5	45	39	8	—
7 HSiMe$_3$	1.30	165	17	<2	27	20	24

[a] Catalyst concentration of ~10^{-5} mol/mol silane. [b] Satisfactory elemental analyses (±0.36% C, H, Si, Cl) were obtained for the products. Silyl group designations in the products are: a = SiCl$_2$Me, b = SiMe$_3$, c = SiCl$_3$. [c] Mol ratio isoprene to silane. [d] Compound IIc present to <5%. [e] Reaction run in a stainless steel vessel. [f] Compound IIIa present in minor amount and included with yield of Ia. [g] Percent yields determined form methylated materials.

IIIa could be detected in the vinyl region of the NMR, which showed a weak, partially obscured resonance on the downfield side of the triplet at δ 5.24 ppm of compound Ia.

Treatment of the 1/1 adduct mixture from the addition of dichloromethylsilane to a 25% excess of isoprene according to Scheme 2, gave 1-trimethylsilyl-3-methylbutane (87%) as the only isolable product. If compound IIIa was present in the original mixture, it was there in too small an amount to be observed after the two step sequence of Scheme 2. This result was obviously misleading since the presence of some IIIa could be detected in the NMR spectrum of the original mixture. Chemical evidence of IIIa was obtained by the inverse addition of methylmagnesium bromide to a mixture of the 1/1 adducts. Coinjection of the olefinic products thus obtained on the Perkin—Elmer 226 Capillary VPC with authentic samples showed the mixture to consist of 48% 1-trimethylsilyl-3-methyl-2-butene (Ib), 43% 4-trimethylsilyl-2-methyl-1-butene (IIb), and 9% *Z*- and *E*-1-trimethylsilyl-2-methyl-2-butene (IIIb). Isolation of the latter mixture would indicate that a minimum of 9% of the 1/1 adducts was formed by a 1,4-addition of dichloromethylsilane to the more hindered side of isoprene.

Addition of trimethylsilane to isoprene was found to be less selective than either that of trichloro- or dichloromethyl-silane. Post [8] reported that trimethylsilane gave no reaction with isoprene and Mamedaliev [9] reported 1,4-addition to the more hindered side. Employing a 30% excess of isoprene and reaction conditions of 165°C for 17 h led to formation of 4-trimethylsilyl-2-methyl-1-butene (IIb, 27%), 1-trimethylsilyl-3-methyl-2-butene (Ib, <2%) and *Z*- and *E*-1-trimethylsilyl-2-methyl-2-butene (IIIb, 19%). This bis adduct, 1,4-bis(trimethylsilyl)-2-methylbutane formed in 24% yield despite the large excess of isoprene. It is also noteworthy that the predominant addition was of the 1,2 mode rather than 1,4 as was observed with trichloro- and dichloromethylsilane. Reduction of the olefinic mixture of 1/1 adducts according to Scheme 2 produced both VI and VII as would be expected in yields of 38 and 18% respectively.

In summary, it would appear that the hydrosilylation of isoprene under chloroplatinic acid catalysis occurs predominantly from the less hindered side which is contrary to literature reports [8]. It should be noted, however, that six different silanes were reported [8] to add in a 1,4-fashion to the more hindered side, while in this work only three of these six compounds were studied. It remains for other workers to recheck the remaining three additions reported [8] with ethyldichlorosilane, benzyldichlorosilane and dibenzylchlorosilane.

Experimental

Routine collection of samples from distillates was done by VPC on an F & M Model 500 chromatograph using a 15′ × 3/8″ 23% QF-1 on Chromosorb P column. Percent yields were determined from peak areas. Isomeric mixtures of totally methylated compounds were analyzed by coinjections with known samples on a Perkin—Elmer Model 226 Capillary Chromatograph. Proton NMR spectra were recorded on a Varian A-60-A Spectrometer and IR spectra were run using a Perkin—Elmer 137 Spectrophotometer. Boiling points of distillates were uncorrected. Elemental analyses (Table 2) were performed by Dr. C.S. Yeh and associates of the Purdue University Microanalytical Laboratory.

TABLE 2

ELEMENTAL ANALYSES OBTAINED OF PRODUCTS

Product	Found (calcd.) (%)			
	C	H	Si	Cl
Ia, IIa, IIIa (mixture)	39.70	6.36	15.45	39.07
	(39.35)	(6.60)	(15.33)	(38.71)
Va	28.26	5.58	19.00	47.77
	(28.20)	(5.41)	(18.84)	(47.56)
Ib, IIb, IIIb (mixture)	67.41	12.68	19.51	—
	(67.52)	(12.75)	(19.73)	
Vb	61.24	12.88	25.70	—
	(61.02)	(13.03)	(25.94)	
Ic, IIc (mixture)	29.43	4.23	13.60	52.50
	(29.50)	(4.46)	(13.80)	(52.25)
Vc	17.92	2.96	16.60	62.50
	(17.71)	(2.97)	(16.57)	(62.74)

The isoprene (Eastman), trichlorosilane (Aldrich), and dichloromethylsilane (Aldrich) were purified by simple distillation before use.

Chloroplatinic acid catalyst solution was prepared by dissolving $H_2PtCl_6 \cdot 6\ H_2O$ (Engelhard) in 2-propanol to a concentration of 0.05 g/ml.

Addition of silanes to isoprene

General procedure

A flame dried, nitrogen purged Carius tube (38 cm × 1.7 cm I.D.) was charged with specified amounts of isoprene, catalyst solution and a silane. The tube was cooled to —78°C, aspirated and sealed by fusing with a flame. The tube was warmed slowly to room temperature and placed in an oil bath at specific temperatures for certain time periods. The products were collected by simple fractional distillation, purified by VPC and identified by their spectra.

(a) Addition of dichloromethylsilane to isoprene. Employing the General Procedure (entry 3, Table 1) and the conditions of Post [8], 10 ml (0.10 mol) of isoprene, 42 μl of catalyst solution and 14.8 ml (0.12 mol) of dichloromethylsilane were placed in the Carius tube. The tube was heated at 165°C for 17 h. Distillation afforded two major fractions: (1) 10.6 g (b.p. 170—173°C); (2) 8.6 g (b.p. 86—89°C at 1.6 mmHg).

The first fraction was composed principally of 1-dichloromethylsilyl-3-methyl-2-butene (51%) and 4-dichloromethylsilyl-2-methyl-1-butene (3%); IR (neat; μ) 6.01 (C=C), 7.94 ($SiCH_3$), 10.08 (C=C); the NMR (Table 3) showed the minor isomer as a weak multiplet at δ 4.84 ppm.

The major component of the high boiling fraction was 1,4-bis(dichloromethylsilyl)-2-methylbutane (25%); IR (neat, μ) 7.98 ($SiCH_3$), 12.0—13.4 (C—C, C—Si); for NMR see Table 3.

(b) The reaction was repeated (entry 4, Table 1) under the same conditions as described in (a) above, but with a 25% excess of isoprene. Distillation yielded two fractions: (1) 32 g (b.p. 163—168°C); (2) 8.3 g (b.p. 92—100°C at 1.9 mmHg). The first fraction consisted of 57% 1-dichloromethylsilyl-3-methyl-2-butene and 31% 2-methyl-4-dichloromethylsilyl-1-butene. The presence of IIIa was

TABLE 3

PROTON NMR SPECTRA OF PRODUCTS

Compound	^1H NMR (δ, ppm)[a]	
	Vinyl[b]	Others[b]
Ia	5.24 (t, J 8, 1H)[c]	0.84 (s, 3H); 1.75 and 1.87 (s, 6H); 2.10 (d, J 8, 2H)
Va	—	0.79 (two s, 6H); 0.94—2.00 (m, 10H).
Ib	5.17 (t, J 8.1, 1H)[c]	0.04 (s, 9H); 1.45 (d, J 8.1, 2H); 1.64 (s, 3H); 1.78 (s, 3H).
IIb	4.70 (m, 2H)	0.06 (s, 9H); 0.69 (m, 2H); 1.78 (s, 3H); 2.03 (m, 2H).
IIIb	5.11 (q, J 6.6, 1H)[c]	0.08 (s, 9H); 1.55, 1.56, and 1.70 (overlapping s, d (J 6.6), and m, 8H).
Vb	—	0.04 and 0.06 (s, 18H); 0.51 (m, 4H); 0.97 (d, J 6, 3H); 1.48 (m, 3H);
Ic	5.15 (t, J 8, 1H)[c]	1.68 (s, 3H); 1.78 (s, 3H); 2.24 (d, J 8, 2H).
Vc	—	1.14 (d, J 6, 3H); 1.21—2.38 (m, 7H).
VI	—	0.02 (s, 9H); 0.52 (m, 2H); 0.92 (d, J 5.8, 6H); 1.30 (m, 3H).
VII	—	0.07 (s, 9H); 0.52 (m, 2H); 0.80—1.68 (m, 9H).

[a] CCl_4 solution with TMS or $CHCl_3$ internal standard (60 MHz); s, singlet; d, doublet; m, multiplet; t, triplet; q, quartet. [b] Single numbers represent center of resonance. [c] Secondary coupling present with $J \leqslant 1.5$ Hz.

observable as a partially buried weak multiplet on the downfield side of the δ 5.13 ppm resonance (1-dichloromethylsilyl-3-methyl-2-butene) The second fraction was mainly the 1,4-bis adduct (9%).

(c) The same procedure as described in (b) above was used except that only 0.5 h of heating was employed (entry 5, Table 1). Substitution of a stainless steel reactor (HOKE ICC-3E-1800) sealed with a capped needle valve gave essentially the same results as the Carius tube runs. The yields were as follows: Carius tube: 58% Ia including IIIa, 34% IIa and 6% bis adduct; stainless steel reactor: 60% Ia including some IIIa, and 32% IIa by NMR integration.

Addition of trimethylsilane to isoprene

Using the general procedure (entry 7, Table 1) the Carius tube, cooled to —78°C, was charged with 15 ml (0.15 mol) isoprene and 55 μl of catalyst solution. This was connected to a tared container of trimethylsilane at —10°C under a nitrogen flow. The trimethylsilane (8.5 g; 0.115 mol) was transferred to the Carius tube by warming. The sealed tube was heated at 160—165°C for 17 h. Distillation gave two fractions: (1) 8 g (b.p. 134—142°C); (2) 5.8 g (b.p. 80—164°C at 20 mmHg). Analysis of the first fraction on the PE-226 Capillary VPC (UCON Polar and SF-96 columns in series) showed four components which were identified by coinjections of authentic materials and spectra as 1-trimethylsilyl-3-methyl-2-butene (Ib; <2%), 4-trimethylsilyl-2-methyl-1-butene (IIb; 27%) and *Z*- and *E*-1-trimethylsilyl-2-methyl-2-butene (IIIb; 20%). Spectra: IIb. IR (neat, μ) 3.30 (H_2C=). 6.10 (C=C), 8.08 ($SiCH_3$); NMR of IIb and IIIb in

Table 3. The second fraction was identified as the 1,4-bis adduct (24%); IR (neat; μ): 3.38 (CH), 8.05 ($SiCH_3$); NMR in Table 3.

Addition of trichlorosilane to isoprene

Employing the general procedure (entry 1, Table 1) and the conditions of Post [8], the Carius tube was charged with 10.0 ml (0.10 mol) of isoprene, 33 μl of catalyst solution and 10.0 ml (0.10 mol) of trichlorosilane. The sealed tube was heated at 165°C for 17 h. Distillation gave two fractions: (1) 14.7 g (b.p. 60—63.5°C at 16 mmHg), (2) 2.8 g (b.p. 97—103°C at 0.9 mmHg). Analysis of the first fraction by VPC (10% SE-30 on Chromosorb A, 9′ × 3/8″ column) showed one major component with a trace of another. Spectral analysis identified the products as 1-trichlorosilyl-3-methyl-2-butene (Ic; 72%) with a small amount of 4-trichlorosilyl-2-methyl-1-butene (IIc); IR (neat; μ): 6.01 (C=C), 12.20 (C=C); the NMR (Table 3) disclosed the minor isomer by a weak multiplet at δ 4.77 ppm. The second fraction contained only the 1,4-bis compound (6%); IR (neat; μ): 3.41 (CH), 13.2—13.8 (C—Si); for NMR see Table 3.

The reaction was repeated with the stainless steel cylinder (entry 2, Table 1) described above. It was charged with 5.0 ml (0.05 mol) of isoprene, 50 μl of catalyst solution and 20.0 ml (0.20 mol) trichlorosilane. The sealed cylinder was heated to 100°C for 0.5 h. Distillation afforded Ic (67%) and the bis adduct Vc (12%) as the only observable products.

Scheme 2

The mixtures of the 1/1 adducts prepared as described above were methylated in the usual fashion with an excess of methylmagnesium iodide. The products were distilled and identified by their spectra and coinjection with known materials on the PE-226. These methylated mixtures were then reduced by the method of Brown [11] with triglyme as solvent. After formation of the intermediate alkylboranes, the mixture was refluxed for 3—6 h before protonolysis with excess propionic acid. The volatiles were distilled and the products were identified by VPC and spectral analysis.

Reduction of trimethylsilane adducts

Using Scheme 2 as described above, 5 g (35.2 mmol) of a 1,2 and 1,4 monoadduct mixture with a 10% excess of reagents gave 3.85 g of volatiles (b.p. to 125°C, not equilibrated) after washing with water to remove excess propionic acid. Analysis on the PE-226 Capillary (SF-96 column) showed two major peaks which were identified as 1-trimethylsilyl-3-methylbutane (VI; 38%) and 1-trimethylsilyl-2-methylbutane (VII; 18%) by coinjection with authentic samples.

Methylation and reduction of trichlorosilane adducts

Methylation of 10 g (0.049 mol) of 1-trichlorosilyl-3-methyl-2-butene (Ic) containing a small amount of 2-methyl-4-trichlorosilyl-1-butene with 0.22 mol of methylmagnesium iodide gave 5 g (65%) of distillate (b.p. 73—78°C at 90 mmHg). The latter was identified as Ib with a trace of IIb by coinjection with known samples; IR (neat; μ) 5.98 (C=C), 7.11 and 7.30 (*gem* CH_3C), 8.07 ($SiCH_3$); see Table 3 for NMR.

Reduction of 4.4 g (30.5 mmol) of the above mixture by the Brown procedure

[11] gave 3.9 g of volatiles (b.p. 110—165°C). Analysis by VPC showed two components, propionic acid and 1-trimethylsilyl-3-methylbutane (VI; 49%). The latter was identified by its IR and NMR spectra.

Methylation and reduction of dichloromethylsilane adducts

Methylation by the usual procedure of 16.5 g (0.09 mol) of a mixture of 65% (Ia) with a trace of another isomer and 35% (IIa) with 0.25 mol CH_3MgI gave 8.7 g of distillate (b.p. 126—131°C) for a 69% yield.

Analysis by VPC showed only the two peaks for Ib and IIb in a ratio of 2.7/1.

Reduction of 2.2 g (15.4 mmol) of this mixture with a 1-fold excess of reagents by the Brown [11] procedure gave 3.9 g of volatiles (b.p. to 112°C; not equilibrated).

Analysis of the distillate by VPC showed propionic acid and a component identified as 1-trimethylsilyl-3-methylbutane (VI, 87%). The IR and NMR spectra matched those of an authentic sample; IR (neat; μ) 7.25 and 7.33 (*gem* CH_3C), 8.03 ($SiCH_3$); NMR (Table 3). The IR spectrum of the isomeric 1-trimethylsilyl-2-methylbutane was considerably different.

A solution of CH_3MgBr (0.218 mol) in diethyl ether was added dropwise in the usual fashion to 18.1 g (0.10 mol) of a mixture of 65% (Ia) with a trace of another isomer and 35% (IIa) from the addition in the stainless steel reactor. Distillation gave 10.3 g of material (b.p. 128—132°C) for a 73% yield.

The NMR spectrum of the distillate showed only those resonances expected from a 60/40 mixture of Ib and IIb. A more detailed analysis was performed by injection on the PE-226 Capillary VPC (UCON Polar and SF-96 columns in series). Four product peaks were observed in a ratio of 13.7/12.2/1.0/1.6. Co-injection with authentic samples showed the second peak to be IIb and the two minor peaks to be *Z*- and *E*-1-trimethylsilyl-2-methyl-2-butene (IIIb). This was the only direct evidence of the formation of 1/1 adducts from the more hindered side of isoprene with dichloromethylsilane. Using the isomer distribution to back calculate gave the following percent yields for the original addition reaction; 45% Ia, 39% IIa, and 8% *Z*- and *E*-1-dichloromethylsilyl-2-methyl-2-butene (IIIa).

Syntheses of authentic samples

1-Trimethylsilyl-3-methyl-2-butenc (Ib). A mixture of 1-chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene in a ratio of 15/1 respectively was prepared [12] in 28% yield. The NMR spectra for each compound agreed with those in the literature [13]. The halides were converted to their respective Grignard reagents in THF and coupled with a 25% excess of trimethylchlorosilane to give 2.3 g (71%) of compound Ib; b.p. 115—142°C, n_D^{20} 1.4299, lit. [14] b.p. 132°C, n_D^{20} 1.4290. The IR and NMR were consistent with the structure.

4-Trimethylsilyl-2-methyl-1-butene (IIb). Trimethylsilylmethylmagnesium chloride was made in the usual fashion from magnesium and trimethylchloromethylsilane (Marstan) in THF and coupled with an equimolar amount of methallyl chloride (Eastman) to give 7.7 g (58%) of compound IIb; b.p. 120—122°C. The NMR spectrum matched that in the literature [10].

Z- and E-1-Trichlorosilyl-2-methyl-2-butene (IIIc). The method of Hetflejš et al. [6] was employed to give a 54% yield of isomeric compounds IIIc; b.p. 160—

164°C, lit. [6] 164—165°C. The NMR spectrum also matched that in the literature [6].

Z- and E-1-Trimethylsilyl-2-methyl-2-butene (IIIb). The isomeric compounds IIIc were methylated in the usual manner with excess methylmagnesium bromide to give 4.1 g (59%) of material (b.p. 126—132°C).

Analysis on the PE-226 Capillary VPC showed three components in a ratio of 3/1/20. The first component was identified as compound Ib by coinjection with a known sample. The last two components were identified by IR and NMR as the isomeric compounds IIIb; IR (neat; μ) 6.01 (C=C), 6.97, 7.10, 7.30, and 7.50 (CCH_3), 8.02 ($SiCH_3$), 10.49 (C=C).

1-Trimethylsilyl-3-methylbutane (VI). This compound was prepared in 63% yield by coupling equimolar quantities of 3-methylbutylmagnesium chloride and trimethylchlorosilane in THF; b.p. 127—131°C, n_D^{24} 1.4056, lit. [15] b.p. 128—129°C, n_D^{25} 1.4052. The IR and NMR were consistent with this structure.

1-Trimethylsilyl-2-methylbutane (VII). This compound was prepared in 57% yield by coupling equimolar quantities of 2-methylbutylmagnesium chloride and trimethylchlorosilane in THF; b.p. 128—132°C, n_D^{24} 1.4086, lit. [15] b.p. 133.5°C, n_D^{25} 1.4097; IR (neat; μ) 3.37 (CH), 6.84, 7.07, and 7.26 (CCH_3), 8.01 ($SiCH_3$), 11.6—12.0 (C—C, C—Si); NMR (Table 3).

Trimethylsilane (VIII). Compound VIII was prepared by the method of Tannenbaum et al. [16].

Acknowledgement

The authors thank the Dow Corning Corporation whose financial support made this work possible.

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