HYDROSILATION OF α,α,α-TRICHLOROALKENES IN THE PRESENCE OF $H_2PtCl_6 \cdot 6H_2O$

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In compounds of the type $CCl_3(CH_2)_nCH{=}CH_2$ (n = 0, 2), hydrosilation (HS) may occur at the multiple bond; in the presence of metal peroxides or carbonyls, the CCl_3 group is reduced to $CHCl_2$ [1]; and, finally, intra- or intermolecular addition of CCl_3 to the multiple bond may take place, as described in [2].

In the present work we investigated the possibility of selective HS of 5,5,5-trichloropentene-1 (I) and 3,3,3-trichloropropene (II) without involving the CCl_3 group. Preliminary experiments showed that the reaction of Et_3SiH with (I) in the presence of tert-butyl peroxide (140°C), $Co_2(CO)_8$ (40°C), or $Fe(CO)_5$ (140°C) does not yield an HS product or hydrogenolysis products. A positive result was obtained by using $H_2PtCl_6 \cdot 6H_2O$; in this case HS occurs at around 20°C, and hydrogenolysis is obtained at 120-140°C (cf. [3] and [4]).

With chloroalkene (I) the reaction proceeds according to the scheme

$$\underset{(I)}{CH_2{=}CH(CH_2)_2CCl_3} + HSiEt_3 \rightarrow \underset{(III)}{Et_3Si(CH_2)_4CCl_3}.$$

Adduct (III) was obtained in 67% yield during complete conversion of (I); Et_3SiCl (0.7%), $(Et_3Si)_2O$ (2.3%), and isomerization products of (I) – Z, E isomers of $CCl_3CH_2CH{=}CHCH_3$ (5% yield) – were also formed.

The reaction with trichloroalkene (II) is much more complex and affords a multicomponent product mixture [yield, % of (II): $CCl_2{=}CHCH_3$ (IV), 55; $CCl_3CH_2CH_3$ (V) 17; $Et_3SiCCl{=}CHCH_3$ (VI), 9; $Et_3SiCH_2CH_2CCl_3$ (VII), 7; $Et_3SiCH_2CH_2CH_2SiEt_3$ (VIII), 0.4]. In addition, Et_3SiCl (39%) and $(Et_3Si)_2O$ (10%) were formed; their yield was calculated on the basis of Et_3SiH. The conversion of Et_3SiH was 79%. The yield of adduct (VII) was insignificant; the major reaction pathway led to the formation of dichloropropene (IV). Special experiments (see experimental section) showed that, under the given reaction conditions, (II) is not rearranged to $CCl_2{=}CHCH_2Cl$ (IX), and (IX) is not reduced to $CCl_2{=}CHCH_3$ (IV). Using dichloroalkenes (IX) and (IV) as examples, it was shown that HS does not take place in compounds with a dichlorovinyl grouping in the presence of $H_2PtCl_6 \cdot 6H_2O$ under selective conditions. Therefore, products (IV)-(VIII) probably are obtained by a scheme analogous to that proposed in [5], including the formation of an intermediate Pt complex with Et_3SiH and alkene.

The structure of starting compounds (I) and (II) and the products of their reaction with Et_3SiH were determined from ^{13}C NMR (Table 1) and PMR (Table 2) spectra. The chemical shifts in the ^{13}C NMR spectra were compared with their hydrocarbon analogs. For triethylalkylsilanes the α, β, and γ effects of the Et_3Si group are similar (± 2 ppm); for alkenesilanes the α and β effects are much larger. According to the PMR data, the ratio of Z and E isomers in chloroalkenesilanes (VI) is 4:1.

EXPERIMENTAL

Trichloroalkenes (I) and (II) were obtained according to [6] and [7], respectively. Their purity was determined by GLC analysis, and their structure was confirmed by ^{13}C NMR spectra. The GLC analysis was performed on an LKhM-8MD chromatograph with a katharometer; carrier gas, He; columns (steel): A) 2 m × 3 mm, 15% SKTFT; B) 2 m × 3 mm, 15% SE-301 on Chromaton N-AW-HMDS (0.16-0.20 mm). For preparative GLC a Tsvet-2 instrument with a preparative adapter was used; steel column, 55 cm × 8 mm, Chromaton N-AW (0.31-0.40) with 10%

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*Deceased.

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TABLE 1. ^{13}C NMR Spectra

Compound		δ, ppm				
		C^1	C^2	C^3	$C^{1'}$ C^4	$C^{2'}$ C^5
$(\overset{2'}{CH_3}\overset{1'}{CH_2})_3Si\overset{1}{CH_2}\overset{2}{CH_2}\overset{3}{CCl_3}$ (VII)		8,3	50,6	102,3	3,0	7,3
$(CH_3CH_2)_3SiCCl{=}CHCH_3$ (VI)	*Z*	136,3	134,9	14,2	2,6	6,9
	E	133,7	139,2	15,7	3,9	6,4
$(CH_3CH_2)_3SiCH_2CH_2CH_2Si(CH_2CH_3)_3$ (VIII) *		16,6	18,5	16,6	3,6	7,4
$(CH_3CH_2)_3SiCH_2CH_2CH_2CH_2CCl_3$ (III)		11,4	23,0	30,4	3,4 55,1	7,3 100,1
$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CCl_3}$ (V)		10,5	48,7	100,0	–	–
$CCl_2{=}CHCH_3$ (IV)		120,8	124,3	14,5	–	–
$CH_2{=}CHCH_2CH_2CCl_3$ (I)		116,5	134,6	30,5	54,2	99,2
$CH_3CH{=}CHCH_2CCl_3$ †	*Z*	13,2	122,4	129,9	54,9	99,8
	E	17,8	123,1	132,7	57,8	98,7

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*J_{C-H} for C^1 and C^3, 116 Hz; for C^2, 127 Hz.

†The spectrum was obtained for fraction I, experiment 1.

TABLE 2. PMR Spectral Parameters of Organosilicon Compounds

Compound		δ, ppm			
		CH_2	CH_3	CCl_3CH_2, CH_3	CH_2, CH=
(III)		0,51 q 0,56 q	0,94 t	2,65 m	1,40 m 1,80 m
(VII)		0,55 q 1,03 q	1,00 t	2,52 m	–
(VIII)		0,51 q	0,94 t	—	1,36 m
(VI) *	*Z*	0,68 q	0,92 t	1,72 d	6,51 q
	E	0,68 q	0,92 t	1,81 d	6,01 q

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*$J^Z_{H,H'} = 6.36$; $J^E_{H,H'} = 7.31$ Hz.

SE-301. PMR and ^{13}C NMR spectra, with and without CH-interaction quenching and using the DEPT method, we obtained on a Brucker WP-200SY spectrometer, with $CHCl_3$ and CCl_4 as standards. PMR spectra were obtained for 30-50% solutions in CCl_4 or $CHCl_3$, with TMS as standard.

5,5,5-Trichloroamyltriethylsilane (III). A mixture of Et_3SiH (105 mmoles) and $CCl_3CH_2 \cdot CH_2CH{=}CH_2$ (70 mmoles) were placed in a three-necked flask equipped with a mixer, reflux condenser, and thermometer. The air in the apparatus was displaced by nitrogen, and 30 drops of 10% $H_2PtCl_6 \cdot 6H_2O$ in $i\text{-}C_3H_7OH$ were added at 20-25°C. The mixture was left at ~20°C for two days, filtered through an Al_2O_3 (1.5 cm) layer, and Al_2O_3 was washed with pentane. After evaporation on an aspirator, 1 g of fraction (I) was obtained; bp, 40-60°C (60 mm). Compound (III) was obtained by vacuum distillation; yield, 67%, 113-114°C (1 mm); n_D^{20} 1.4756; d_4^{20} 1.0634; found (%): C, 45.74; H, 8.32; Si, 9.31; Cl, 36.86 ($C_{11}H_{23}Cl_3Si$); calculated (%): C, 45.59; H, 8.00; Si, 9.69; Cl, 36.71. For ^{13}C NMR spectra, see Tables 1 and 2. In addition, Et_3SiCl (0.7%) and $(Et_3Si)_2O$ (2.3%) were isolated. The PMR spectrum of fraction (I) was as follows (δ, ppm): 1.77, d (CH_3); 3.27, d, and 3.37, d (Z, E-CH_2); 5.5-5.9 (CH=CH).

Reaction of $CCl_3CH{=}CH_2$ with Et_3SiH. In an analogous manner, Et_3SiH (300 mmoles), $CCl_3CH{=}CH_2$ (150 mmoles), and $H_2PtCl_6 \cdot 6H_2O$ (30 drops), after distillation, yielded the following fractions: I, 30-69°C (60 mm), 26.7 g; II, 40-49°C (15 mm), 11.7 g; III, 56-95°C (2 mm), 13.9 g; residue, 0.8 g. The compounds $CCl_2{=}CHCH_3$ (IV) and $CCl_3CH_2CH_3$ (V) were isolated from fraction (I) by distillation. Et_3SiCl was isolated from fraction (II), and the following compounds were obtained from fraction (III) by preparative GLC: a mixture of E and Z isomers of $Et_3SiCCl{=}CHCH_3$ (VI), $Et_3SiCH_2CH_2CCl_3$ (VII) (cf. [8]), $(Et_3SiCH_2)_2CH_2$ (VIII) (cf. [9]), and $(Et_3Si)_2O$. The yields of compounds (IV)-(VIII) are given in the general section; NMR spectra are shown in Tables 1 and 2. The following data were obtained for E, Z-(VI) isomers: Found (%): C, 55.96; H, 9.93; Si, 14.73; Cl, 18.70 ($C_9H_{19}SiCl$); calculated (%): C, 56.66; H, 10.04; Si, 14.72; Cl, 18.58.

Reaction of Et_3SiH with $CCl_2{=}CHCH_2X$ (X = H, Cl). In an analogous manner, Et_3SiH (28 mmoles), $CCl_2 = CHCH_2X$ (14.2 mmoles), and $H_2PtCl_6 \cdot 6H_2O$ (3 drops) afforded, after distillation, Et_3SiH (83%), $CCl_2 = CHCH_2X$ (96%), and Et_3SiCl (3%). AT X = H, $Et_3SiCCl{=}CHCH_3$ (1%), and $(Et_3Si)_2O$ (0.4%) were also obtained.

CONCLUSIONS

1. In the presence of $H_2PtCl_6 \cdot 6H_2O$, Et_3SiH is readily added to 5,5,5-trichloropent-1-ene at room temperature.

2. Reaction of $CCl_3CH{=}CH_2$ with Et_3SiH gives $CCl_2{=}CHCH_3$ as the main reaction product.

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DEMERCURATION OF SECONDARY—BENZYLIC TYPE ORGANOMERCURY COMPOUNDS IN METHANOL AND NITROMETHANE

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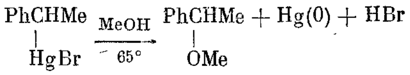
Based on the results of a study of the solvolytic demercuration of 1-(8-quinolyl)ethylmercuric bromide in methanol [1, 2], a radical mechanism has been proposed for this reaction. In the present paper we have sought to expand the range of benzylic organomercury compounds which have been studied, and also to obtain direct evidence for the radical character of the reaction process. Toward this end, another secondary—benzylic type organomercury system was selected for study, namely, 1-phenylethylmercuric bromide. It was found that this compound behaves the same as the previously investigated compound, 1-(8-quinolyl)ethylmercuric bromide, under the conditions of solvolytic demercuration. It is readily demercurated upon refluxing in methanol, generating elemental mercury and the methyl ether of phenylmethylcarbinol in nearly quantitative yields. Secondary—benzylic organomercury compounds (OMC)



$$\underset{\displaystyle HgBr}{PhCHMe} \xrightarrow[65^\circ]{MeOH} \underset{\displaystyle OMe}{PhCHMe} + Hg(0) + HBr \qquad (1)$$

undergo facile demercuration even upon heating in an aprotic solvent such as nitromethane. The product composition for these reactions is given in Table 1. No traces of reaction are seen, however, in benzene solution at 80°C after 15 h.

EPR spectroscopy proved useful in detecting the radical particles formed as a result of

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