

## CATALYSIS BY METAL COMPLEXES. XII.\*

## SELECTIVE PREPARATION OF 1- AND 2-TRICHLOROSILYL-1-PHENYLETHANE BY HYDROSILYLATION

M. ČAPKA, P. SVOBODA and J. HETFLJEŠ

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

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The title compounds were prepared selectively in high yields under mild conditions by hydrosilylation of styrene with trichlorosilane catalysed by  $\text{Ni}(\text{CO})_4$  and  $\text{H}_2\text{PtCl}_6-(\text{C}_6\text{H}_5)_3\text{P}$  (1 : 1 molar ratio), respectively. The procedure can also be used to prepare the methyldichlorosilyl derivatives. The effect of several cocatalysts upon selectivity of the addition is reported.

Of several methods so far reported for preparing 1- and 2-trichlorosilyl-1-phenylethane<sup>1-4</sup> the most convenient and most versatile one seems to be hydrosilylation<sup>3,5-10</sup>. The published hydrosilylation procedures suffer, however, from certain disadvantages which stem from the fact that they require the use of solvents<sup>5</sup>, of less accessible catalysts<sup>8-10</sup>, or are non-selective<sup>6,7</sup>, yielding a mixture of both isomeric adducts which can be separated only with difficulty by careful fractionation.

These circumstances, along with our continuing interest in hydrosilylation of substances containing conjugated double bonds (*cf.*<sup>10</sup> and references therein), led us to seek for catalysts (catalytic systems) which would enable selective formation of the title compounds and would be readily available for preparative purposes. We have found that in the presence of nickel tetracarbonyl, the addition of trichlorosilane to styrene proceeds smoothly at room temperature, affording 1-trichlorosilyl-1-phenylethane ( $\alpha$ -adduct), as a sole reaction product. The best yields were obtained with equimolar amounts of the reactants. During the reaction a catalytically active nickel complex is slowly decomposed to black metallic nickel, the decomposition being faster on using an excess of the silicon hydride (or on adding the hydride first to the catalyst). The addition of a stabilizing ligand such as triphenylphosphine slows down this decomposition in the expense of the activity of the catalyst. Thus, for example, when an equimolar mixture of the reactants was maintained in the presence of  $\text{Ni}(\text{CO})_4 + (\text{C}_6\text{H}_5)_3\text{P}$  (1 : 2 molar ratio) at room temperature for 1 day, the  $\alpha$ -adduct was formed in only 50% yield. Other phosphorus-containing ligands exerted similar effect ( $(\text{C}_4\text{H}_9)_3\text{P} - 30\%$  yield;  $(\text{C}_6\text{H}_5\text{O})_3\text{P} - 25\%$  yield; used in 1 : 1 molar ratio with respect to the

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nickel carbonyl). The nickel carbonyl-phosphine complexes,  $\text{Ni}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$  (ref.<sup>11</sup>) and  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$  (ref.<sup>12</sup>), were slightly active even at the higher temperature (80°C, 2 h; 10% and 3% yield of the  $\alpha$ -adduct, respectively). With methyl-dichlorosilane, due to its lesser reactivity, good yields of the corresponding  $\alpha$ -adduct were obtained at an elevated temperature. As to its activity and selectivity, nickel tetracarbonyl is thus comparable with a carbonyl-cyclopentadienyl-nickel complex, one of the most efficient catalysts for this reaction<sup>10</sup>.

Selective preparation of the other isomer, 2-trichlorosilyl(methyldichlorosilyl)-1-phenylethane ( $\beta$ -adduct) was effected with a catalytic system consisting of chloroplatinic acid and triphenylphosphine. The effect of the cocatalyst upon selectivity of the additions is shown in Table I. As follows from the table the relative amount of the isomers formed depends in part also on the structure of starting silicon hydride. The lesser sensitivity of the reaction of methyldichlorosilane with styrene towards the effect of solvent was already observed by Musolf and Speier<sup>6</sup>. The authors reported that the addition of 2 vol.% of tetrahydrofuran in respect to the olefine in the reaction of trichlorosilane led to the exclusive formation of the  $\beta$ -trichlorosilyl derivative, while in the case of methyldichlorosilane both isomers were formed in the ratio  $\alpha/\beta = 19/81$ . When compared with tetrahydrofuran, triphenylphosphine exhibits remarkable directing effect. The  $\beta$ -methyldichlorosilyl derivative was selectively

TABLE I

The Effect of Cocatalysts upon Selectivity of  $\text{H}_2\text{PtCl}_6$ -Catalyzed Hydrosilylation of Styrene

15 mmol of styrene, 15 mmol of silicon hydride, 0.03 ml of 0.01M- $\text{H}_2\text{PtCl}_6$  in 2-propanol, 80°C, 2 h (sealed ampoules).

Cocatalyst $\text{H}_2\text{PtCl}_6^a$	The yield (%) <sup>b</sup> of $\alpha/\beta$ adducts in the presence of <sup>c</sup>			
	TPP	BDA	Py	PAN
	$\text{HSiCl}_3^d$			
1	0/95	0/85	0/92	36/64
2	0/88	0/80	0/90	27/73
	$\text{CH}_3\text{SiHCl}_2^e$			
1	5/93	4/95	30/69	32/67
2	0/99	5/89	27/72	32/67
3·3	0/0 <sup>f</sup>	—	0/72	33/66

<sup>a</sup> Molar ratio, cocatalysts added as 0.01M solutions in benzene, <sup>b</sup> determined by g.l.c., <sup>c</sup> TPP triphenylphosphine, BDA benzyldimethylamine, Py pyridine, PAN phenylacetoneitrile, <sup>d</sup> in the absence of cocatalysts the yield of  $\alpha/\beta$  adducts was 38.5/58.7 (cf.<sup>6</sup>), <sup>e</sup> in the absence of cocatalysts the yields of  $\alpha/\beta$  adducts was 34.5/64.5 (cf.<sup>6</sup>), <sup>f</sup> at 110°C (2 h) the yields of  $\alpha/\beta$  adducts was 0/95.

formed already at the cocatalyst/ $H_2PtCl_6$  molar ratio 2. Under otherwise identical conditions the higher relative amount of the cocatalyst inhibited the reaction (Table I; see however footnote<sup>e</sup>).

It is noteworthy that also other well coordinating ligands, such as benzyldimethylamine and pyridine (Table I) exerted a similar effect, even though less pronounced in the reaction of methylchlorosilane. Phenylacetonitrile, a weakly coordinating ligand, had in both cases only slight selectivity-enhancing influence.

## EXPERIMENTAL

*Trichlorosilane and methylchlorosilane* were supplied by VCHZ Synthesia (Kolín), and were used without further purification. Styrene, stabilized by 2,6-di-*tert*-octylpyrocatechol, was donated by the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague. Chloroplatinic acid was a product of Kovohutě Works (Vestec) and nickel tetracarbonyl was supplied by Fluka A.G.. Gas chromatographic analyses were carried out under conditions described in a previous work<sup>10</sup>. Authentic samples of isomeric trichloro- and methylchlorosilylphenylethanes were prepared by independent method. The structure of the products was confirmed by IR and NMR spectroscopy.

*1-Trichlorosilyl-1-phenylethane*. A mixture of 5 ml (43 mmol) of styrene, 5 ml (49 mmol) of trichlorosilane and 0.1 ml (0.8 mmol) of nickel tetracarbonyl was stirred under argon for 1 h. Distillation through a short column afforded 10 g (97% yield) of chromatographically pure product, b.p. 226–230°C (ref.<sup>13</sup> records b.p. 225–228°C/753 Torr).

*1-Methylchlorosilyl-1-phenylethane*. A mixture of 5 ml (43 mmol) of styrene, 5 ml (47 mmol) of methylchlorosilane and 0.1 ml (0.8 mmol) of nickel tetracarbonyl was refluxed under argon for 4 h. Distillation afforded 8.3 g (88% yield) of chromatographically pure product, b.p. 114 to 120°C/20 Torr (ref.<sup>14</sup> records b.p. 121–122°C/25 Torr).

*2-Trichlorosilyl-1-phenylethane*. A reaction flask placed in an oil bath heated to 80°C was successively charged under argon with 0.3 ml of 0.01M solution of chloroplatinic acid in 2-propanol, 0.3 ml of 0.01M solution of triphenylphosphine in benzene, 15.6 g (0.15 mol) of styrene and 20.3 g (0.15 mol) of trichlorosilane. During 1 h the temperature of the bath was gradually raised to 150°C. Distillation of the reaction mixture under reduced pressure yielded 32.2 g (81% yield) of chromatographically pure product, b.p. 115–120°C/15 Torr (ref.<sup>13</sup> records b.p. 93–96°C/3 Torr).

*2-Methylchlorosilyl-1-phenylethane*. A mixture of 0.3 ml of 0.01M solution of chloroplatinic acid in 2-propanol, 0.8 ml of 0.01M solution of triphenylphosphine in benzene, 15.6 g (0.15 mol) of styrene and 17.3 g (0.15 mol) of methylchlorosilane placed under argon in a sealed glass ampoule was heated to 90°C for 2 h. The next day the reaction mixture was distilled to give 22.7 g (69% yield) of chromatographically pure product, b.p. 106–110°C/10 Torr (ref.<sup>8</sup> records b.p. 108°C/11 Torr).

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